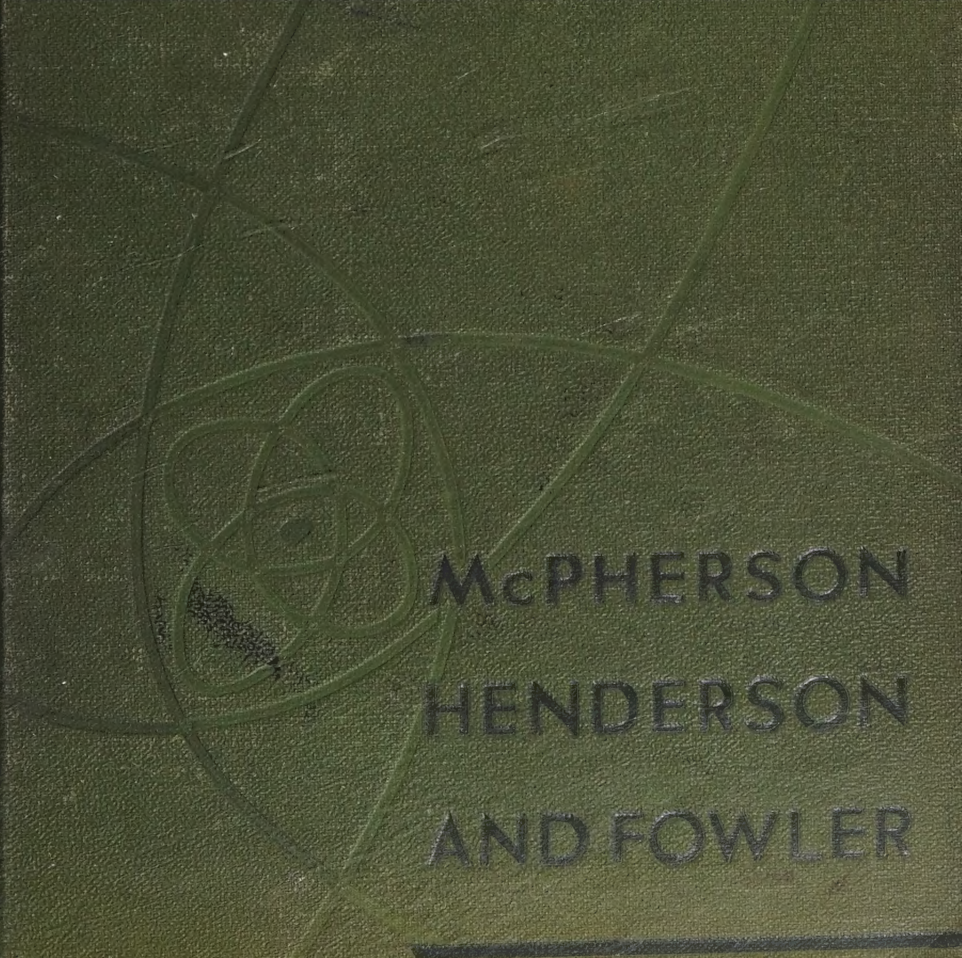
CHEMISTRY FOR TODAY



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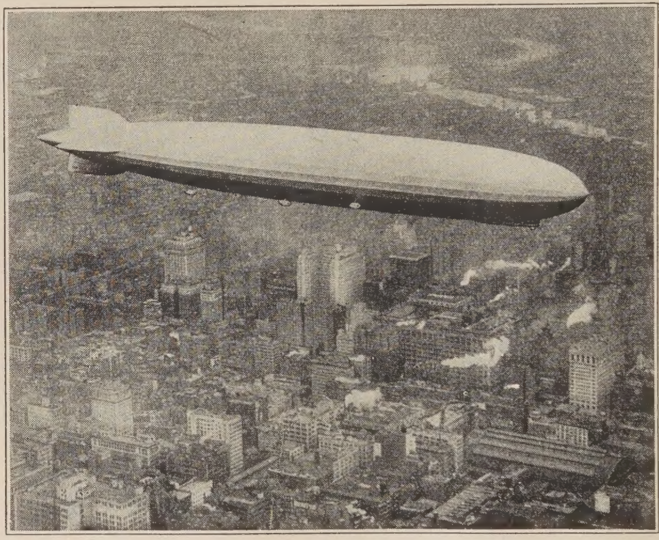

View of the *Graf Zeppelin* over Philadelphia on August 8, 1929, just before starting on her Long Journey around the World

The chemist has made many contributions to the development of airships, or Zeppelins, as they are often called for their inventor. The picture shows the *Graf Zeppelin* just before leaving the United States on her trip around the world. With a crew of 40 men and a passenger list of 16, the ship left Lakehurst, New Jersey, August 8, 1929, stopping at Friedrichshafen (Germany), Tokyo (Japan), and Los Angeles, and returned to Lakehurst on August 29. Although 21 days thus elapsed between the date of leaving Lakehurst and the date of returning, the total number of days of actual flying was just under 12. The *Graf Zeppelin* is 770 feet in length. Its framework is constructed of a light alloy of aluminum. In its journey around the world, the ship was inflated with hydrogen, the lightest of all gases. This gas, however, has the disadvantage of being very inflammable, so that in the United States it is being replaced by helium as an agent for the inflation of airships; for, while helium is about twice as heavy as hydrogen, it possesses the very great advantage of being noncombustible and hence much safer to use

A TEXTBOOK FOR SECONDARY SCHOOLS

CHEMISTRY FOR TODAY

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PREFACE

In writing a textbook in chemistry every author will endeavor to produce one that, in his judgment, makes very clear the underlying laws and theories which constitute the fabric of the science; that reflects with accuracy its progress; that makes a happy selection from the wealth of practical applications crowding for attention; and that lends itself readily both in the classroom and in the laboratory to the methods and ideals of the progressive teacher. This, at least, is what the present authors have attempted.

To the teachers using this book the authors wish to emphasize the conviction expressed in earlier texts that the practical applications of chemistry have a place in high-school instruction largely in so far as they are used to illustrate the principles of the science and the way in which chemical knowledge can be turned to the uses of society. The main object of the course in chemistry must always be *to train young people to think and to imagine in the realm of chemical facts and laws,* and the teacher who finds at the end of the course that his pupil has acquired what seems to be a fund of useful information, but has little ability to think for himself how he would solve a simple chemical problem, should feel dissatisfied with his effort.

This text is an outgrowth of "Chemistry and its Uses," embodying the fundamental features of that book but including so many new features that in reality it is a new text. The increase in the number of pages is not due to an extension of subject matter but to a more ample explanation of difficult things, to the use of a larger number of illustrations, and to the fact that the text is set in one size of type, much additional information being given in the legends of the photographs and diagrams.

The subtitle of many chapters, as well as the introductory paragraph, has been written with the intent to stimulate interest in what is to follow — a motivating appeal, as it were.

In a *qualitative* sense formulas and equations have been introduced very early so that the student may at the outset begin to learn the chemist's shorthand language. When a sufficient foundation has been laid the *quantitative* meaning is developed.

The solar-system picture of atomic structure, with valence electrons in uncompleted outer orbits, has been freely used. The authors are well aware of the many objections to this idea — and indeed to any picture of atomic structure; but it seems much better, as well as entirely scientific, to use a defective simple picture until we have a convincingly better one.

We have given the story of alchemy more fully as an introductory chapter, knowing well that many teachers may not have the time to make class assignments of this material, but in the hope that the students will read the chapter and learn a little about where the science of chemistry came from and how young it is.

A great deal of thought has been given to the matter of questions and problems, and a somewhat new plan has been adopted to provide for individual differences within the class. The questions are arranged in three groups, as follows:

1. *Chapter Summary in Question Form.* The questions contained in this list are largely objective in form, although other type questions are included. These questions, when properly answered, constitute an outline of the minimum essentials of the chapter as scheduled by the College Entrance Examination Board and by the syllabus of the New York Regents. They are primarily for the self-testing of the student. By answering these questions, the student will test his own knowledge of the subject and at the same

time construct for himself an outline of minimum essentials, which the authors believe is a much better plan than to provide such an outline for him. The answers to the questions are given directly in the text.

2. *Thought Questions.* The questions in this list are supplementary to those contained in the first list and differ from the latter in that the answers to the questions are not usually given directly in the text. Any thoughtful student who has mastered the material contained in the text will have no difficulty in answering the questions in this list.

3. *For Honor Students.* In this list are gathered a few more difficult questions, problems, projects, and suggestions for themes, which are intended to appeal to the student notably interested in the subject and willing to test his strength. It is not expected that any one student will complete all the projects listed or write all the themes suggested; he is to select one (or more) of special interest to him or assigned to him by the teacher.

In the Appendix will be found a list of suitable books, popular in style, that will appeal to students of chemistry. A minimum of at least the five of these books designated by a double asterisk in the list should be available to the students in every high school that includes chemistry in its curricula. Under the heading "For Honor Students" in certain chapters of the text, references are made to one or more of these five books. An occasional reference is also made to any encyclopedia, which presumably is available in every high school.

Finally, we wish to express our deep sense of obligation to many former students, colleagues, industrial chemists, and business firms, who almost without fail have responded to our requests for information or for illustrative material.

THE AUTHORS

CONTENTS

CHAPTER PAGE

INTRODUCTORY. ALCHEMY, THE PARENT OF MODERN CHEMISTRY 3

I. WHAT CHEMISTRY IS, AND WHAT THE CHEMIST DOES 9

II. MATTER AND ITS KINDS 18

III. OXYGEN · THE MOST ABUNDANT OF ALL THE ELEMENTS 32

IV. HYDROGEN · THE LIGHTEST OF ALL ELEMENTS 51

V. STATES OF MATTER · SOLID, LIQUID, GASEOUS 62

VI. WATER · THE MOST IMPORTANT LIQUID IN THE WORLD 76

VII. THE COMPOSITION OF WATER; HYDROGEN PEROXIDE 84

VIII. SOLUTIONS 96

IX. MOLECULES AND ATOMS · NEXT TO THE SMALLEST THINGS IN CHEMISTRY 108

X. FORMULAS, EQUATIONS, PROBLEMS · NEW MEANINGS FOR SYMBOLS AND FORMULAS 120

XI. CARBON · AS DIAMOND A COSTLY LUXURY; AS COAL A CHEAP NECESSITY 135

XII. THE TWO OXIDES OF CARBON · THE ONE PUTS OUT FIRE; THE OTHER BURNS 145

XIII. VALENCE · HOW ATOMS FIT TOGETHER 158

XIV. THE STRUCTURE OF THE ATOM · EACH ATOM A LITTLE SOLAR SYSTEM 165

XV. CHLORINE; HYDROGEN CHLORIDE; HYDROCHLORIC ACID 177

XVI. SODIUM AND POTASSIUM · METALS THAT ARE LIGHTER THAN WATER 192

XVII. ACIDS, BASES, AND SALTS · THE THREE MOST IMPORTANT GROUPS OF COMPOUNDS 200

XVIII. IONIZATION · WHY SOLUTIONS CONDUCT THE ELECTRICAL CURRENT 210

XIX. NITROGEN AND SOME RARE GASES · GASES THAT ACT WITH DIFFICULTY OR NOT AT ALL 221

XX. THE ATMOSPHERE · AN OCEAN OF GAS SURROUNDING THE EARTH 229

CHAPTER PAGE

XXI. SOME OF THE SIMPLER COMPOUNDS OF NITROGEN . . 237

XXII. REVERSIBLE REACTIONS; EQUILIBRIUM · REACTIONS THAT GO IN EITHER DIRECTION 254

XXIII. SULFUR AND THE SULFIDES · A FAMILIAR ELEMENT WITH MANY USES 262

XXIV. THE OXIDES OF SULFUR AND THEIR ACIDS · TWO COMPOUNDS WITH VERY IMPORTANT NEAR RELATIVES 273

XXV. THE PERIODIC LAW · FAMILY GROUPS OF SIMILAR ELEMENTS 286

XXVI. THE CHLORINE FAMILY · A FAMILY OF FOUR VERY SIMILAR ELEMENTS 297

XXVII. THE PHOSPHORUS FAMILY 306

XXVIII. SOILS AND FERTILIZERS 316

XXIX. SILICON AND BORON · ONE VERY IMPORTANT ELEMENT AND ANOTHER THAT HAS FEW USES 322

XXX. SILICATE INDUSTRIES · GLASS, CLAY PRODUCTS, ENAMELS, CEMENT 331

XXXI. THE COLLOIDAL STATE · THE CHEMISTRY OF VERY SMALL PARTICLES 339

XXXII. PETROLEUM AND THE COMPOUNDS THAT COMPOSE IT . 350

XXXIII. SOME FUELS AND RELATED TOPICS 359

XXXIV. ORGANIC COMPOUNDS — COMPOUNDS OF CARBON . . . 372

Part I. The Carbohydrates 372

Part II. The Alkaloids 383

Part III. The Alcohols 384

Part IV. Organic Acids and their Derivatives . . . 391

Part V. Soaps 396

Part VI. Coal-Tar Compounds 399

Part VII. Foods 406

XXXV. THE METALS · THE MAIN SUPPORTS OF AN INDUSTRIAL AGE 415

XXXVI. THE ALKALI METALS · METALS WHOSE COMPOUNDS SERVE US DAILY 424

XXXVII. CALCIUM AND ITS RELATIVES 440

XXXVIII. MAGNESIUM, ZINC, AND CADMIUM 452

XXXIX. ALUMINUM 462

XL. HOW WE PURIFY AND SOFTEN NATURAL WATERS ON A LARGE SCALE 476

CHAPTER PAGE
XLI. IRON AND TWO CLOSELY RELATED METALS 482
XLII. COPPER, MERCURY, AND SILVER; PHOTOGRAPHY 503
XLIII. TIN AND LEAD; PAINTS 519
XLIV. GOLD AND PLATINUM 532
XLV SOME LESS FAMILIAR ELEMENTS 538
XLVI. THE STORY OF RADIUM 547

APPENDIXES

A. CHEMICAL LIBRARY 557
B. THERMOMETERS 559
C. REDUCTION OF GAS VOLUMES TO STANDARD CONDITIONS . 561
D. SOLUBILITIES OF SOME OF THE COMPOUNDS OF THE METALS 566
E. TABLES · DENSITIES AND MELTING POINTS OF SOME COMMON ELEMENTS · SOLUBILITY OF VARIOUS SOLIDS · PRESSURE OF AQUEOUS VAPOR 567
F. REFERENCE TABLES · WEIGHT OF 1 LITER OF VARIOUS GASES · ELECTROCHEMICAL SERIES · RELATION BETWEEN ENGLISH AND METRIC CONSTANTS 568
INDEX 569
REFERENCE TABLES . . . . Facing Inside Back Cover
TABLE OF ELEMENTS . . . . Inside Back Cover

CHEMISTRY FOR TODAY

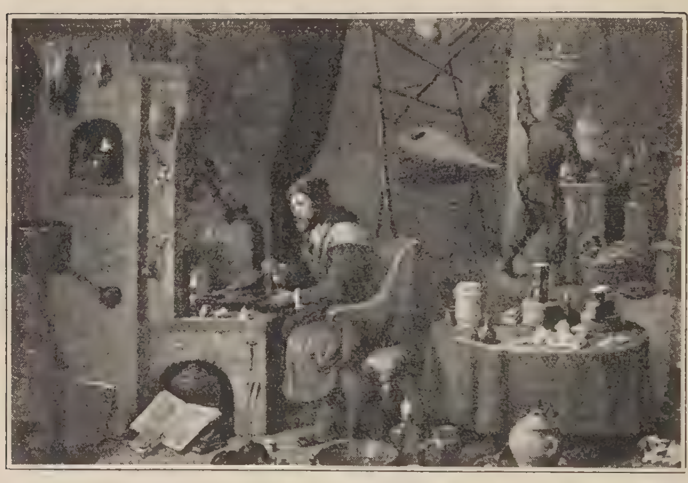

FIG. 1. An alchemist at his work and some of his appliances

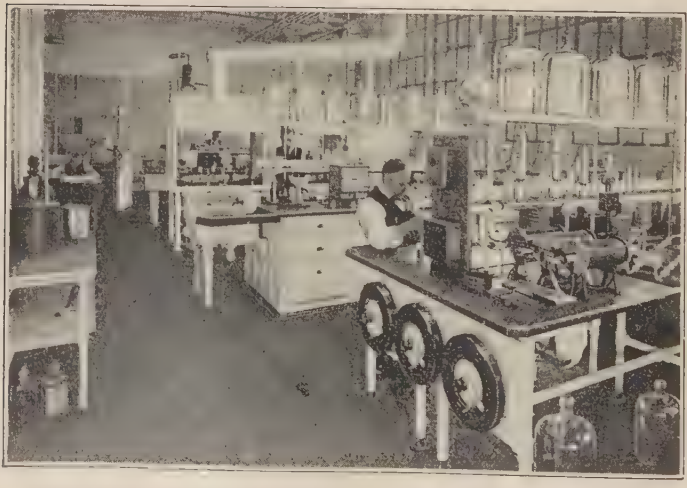

FIG. 2. A typical laboratory of a modern automobile plant

INTRODUCTORY CHAPTER

ALCHEMY, THE PARENT OF MODERN CHEMISTRY

Introduction. The Middle Ages were full of mysteries and wonder-working; many marvelous things were described but very little was really understood. Among these wonder-workers the alchemist was a central figure. Who has not seen him pictured with white beard amid the mysterious vessels of his dark art in his secret workshop (Fig. 1)? Who was he, and what were some of his beliefs and achievements?

The alchemist. The chemist is really a very modern man, not much more than two hundred years old. All his ancestors of the Christian Era may properly be called alchemists, especially those of the Middle Ages, and the knowledge they handed down to their chemical child was gained very slowly through a good many thousands of years. A brief account of the ideas of these old alchemists is a very fitting introduction to the study of chemistry.

The primitive metals. Since the dawn of history man has been greatly concerned with the finding, the production, and the use of metals. When Columbus discovered America, not more than nine or ten metals were known, and of them six had been widely used for at least four thousand years, namely, gold, silver, copper, lead, tin, and iron. Some of these, such as gold, were found as metals in nature; while others were prepared from heavy colored stones or *ores* by ways that must have taken thousands of years to discover and develop; for such methods were due in the first instance to chance, and were very slowly improved.

Transmutation of metals. The ancients gradually came to the opinion that iron ore was simply impure iron, and that the preparation of iron from its ores was a process of *purification*, or refining. They reasoned that if they should purify iron still further, very likely it would become still heavier and more valuable, and would so be transformed into copper or silver or finally gold, which was regarded as completely pure metal.

They did not regard the metals they knew as entirely different things, but as different stages in purity. This purification of one metal into another was called the *transmutation* of the metals; and to accomplish it was one of the great endeavors of the alchemist of the Middle Ages. Many royal courts employed alchemists who claimed that they could change the cheaper metals, such as iron, into gold.

Transmutation a reasonable belief. There were a number of facts that tended to make a belief in transmutation reasonable. Three thousand years before Christ men had learned to melt copper with a little tin and so make *bronze*. This was harder than copper, resembled gold in color, and appeared to be a new metal, yet they knew it to be impure copper. Many ores, as we now know, contain two distinct metals, such as lead and silver. In working with such an ore they first obtained what seemed to be pure lead; yet by certain refining processes some silver could be recovered from this lead. They thought the lead had changed into silver.

The "elements" of the Greeks. In the golden age of Greece the life of the learned teachers, or philosophers, was far removed from the practical activity of the workshop. These philosophers spun theories out of their minds with little knowledge of practical things. They were more interested in what an object looked like and how it felt to the touch — what we should call some of the *properties* or *qualities* of matter — than in the question of what it was made.

So they classified objects as being cold or warm, wet or dry, heavy or light. They called these *qualities* the "elements" of matter, just as we sometimes speak of the elements of arithmetic or geography, meaning fundamental principles, and they classified these elements as four in number:

1. *Fire:* the property of dryness and warmth.
2. *Air:* the property of wetness and warmth (or of being a gas).
3. *Earth:* the property of dryness and cold (or of being a solid).
4. *Water:* the property of wetness and cold (or of being a liquid).

The philosophers taught that any given object or material was a mixture or blending of these four "elements" in various proportions, really meaning that the object could be described in these terms.

Effect of Greek ideas on alchemy. As Greek learning waned, the more ignorant practical workshop men took these philosophical ideas as *fact,* and came to believe that any given material, such as a metal or a stone, was made up of fire, air, earth, and water, in some definite proportion, and that by changing the proportion you could change one metal or one stone into another.

Alchemists of the Middle Ages. During the Middle Ages the alchemists began to differ among themselves as to what things should be regarded as so-called "elements." Sulfur, quicksilver, and salt were sometimes preferred to earth, air, fire, and water. They wrote (usually in Latin) about their discoveries in very vague, mysterious language which is difficult to interpret and sometimes appears to be purposely misleading. Thus: "I asked him what was the color of the king. He replied that he was dressed in cloth of gold, with a doublet of black velvet, a shirt as white as snow, but his skin as red as blood." This means that in preparing the philosopher's stone (see next paragraph), the solutions used were successively black, white, and red. Extensive use was made of symbols in picture form. The metals were represented by symbols of the planets, including the sun and moon, or by animals (Figs. 3 and 4).

The philosopher's stone. Failure followed all honest efforts to change one metal into another (though many fraudulent processes were described) or to produce any well-known substance by making mixtures of the so-called elements. As a result, a belief gradually grew up that these changes could be brought about only by the wonderful power of a magical substance known as "the philosopher's stone," and many ways were described for preparing this wonderful substance (Fig. 4). Mere touch of this stone would transform untold quantities of common metals into gold, cure diseases, and give perpetual youth to its fortunate possessor. It was like Aladdin's lamp in the Arabian Nights. By the eighteenth century alchemy was fast becoming a disreputable art, for the revival of learning and the breaking away from old traditions made such ideas ridiculous.

Results of alchemy. While alchemy completely failed in its main effort, it resulted in bringing to light a great deal of useful information. The alchemists discovered a few new metals such as zinc and antimony and a considerable number of useful chemical substances such as acids and drugs, improved such industries as metallurgy, glass-making, enameling, and dyeing, and invented many processes such as distilling and methods of filtering and grinding.

Phlogiston. By the beginning of the eighteenth century the vain quest for the philosopher's stone was being given up, and men were greatly interested in a very practical question; namely, What makes some things burn while others will not burn? The best answer they could find was this: A burnable body contains a peculiar invisible

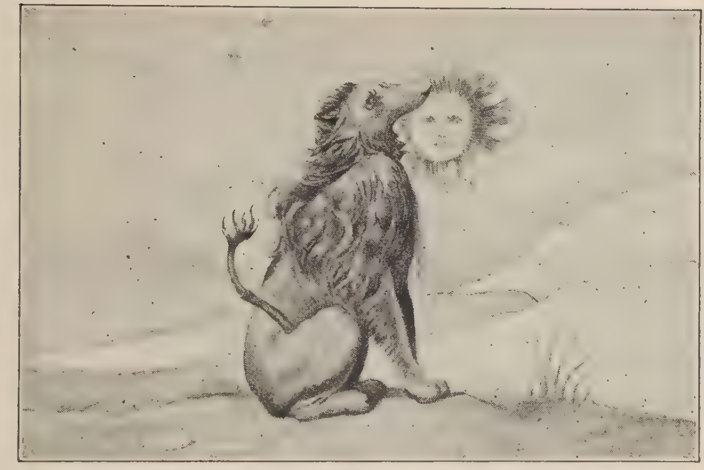

FIG. 3. The lion (mercury) devouring the sun (gold) — mercury dissolving gold

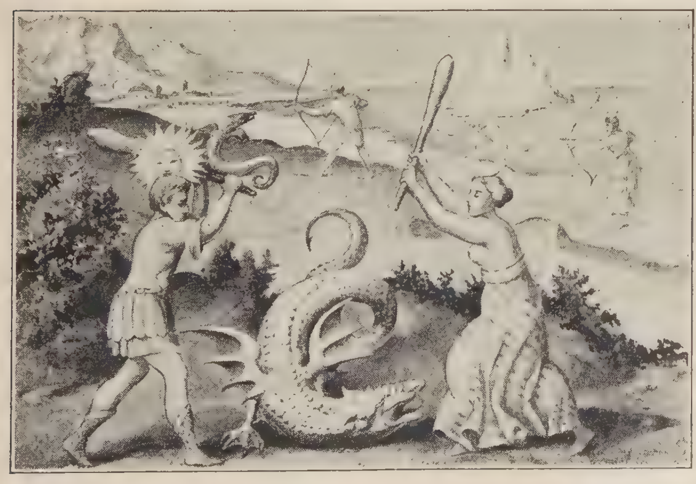

FIG. 4. Gold (the sun) and silver (the moon) being combined with mercury (the dragon) in making the philosopher's stone

gas called *phlogiston*. When the body burns, the phlogiston escapes, causing crackling, small explosions, sparks, flame, and smoke. The ash that remains they called the *calx*. When a metal such as iron burns, the calx is the iron minus the phlogiston which it contained before burning. Evidently the calx should weigh less than the iron, but in reality it weighs more. Many such objections to phlogiston arose, and chemists began to search for a more satisfactory explanation of burning.

Discovery of oxygen. In 1774 (just before the beginning of the American war for independence) an Englishman, Joseph Priestley, discovered oxygen, and it became possible not only to give a satisfactory explanation of burning, but to lay the foundations of chemistry as we have it today. The discovery of oxygen is sometimes thought of as marking the beginning of chemistry in contrast with all the alchemistic endeavor of long centuries, but it should be remembered that chemistry inherited much valuable knowledge from the hard-working alchemists.

CHAPTER I

WHAT CHEMISTRY IS, AND WHAT THE CHEMIST DOES

1. *Introduction.* What is chemistry? What does the chemist work with, and for what purpose? How is chemistry related to manufacturing, and to other studies, such as physics, agriculture, medicine? These are some of the questions that come to mind as one begins the study of chemistry.

2. What chemistry is. Very wonderful changes in matter take place before our eyes every day to which we pay little attention. Nearly all metals tend to rust, losing their bright luster and changing into material that looks like earth rather than metal; coal and wood burn, producing gases and ashes; in the motor car, gasoline burns, producing great quantities of gases, but we are usually more interested in the motion of the car than in these changes in the gasoline; growing plants take up materials from the soil and the air and form from these the vast variety of things we get from plants and trees; our bodies digest the food we eat, using a part as fuel and changing a part into bone, muscle, and other structures of the body.

In all these examples *the materials with which we start are changed into others of entirely different composition.* Chemistry deals with all such changes as these, so that we may define the science of chemistry as follows: *Chemistry deals with all those changes in materials that result in altering the composition of the materials.*

Of course one may break a dish in pieces, or crush a lump of coal into fragments, or file a piece of iron into powder, without changing the composition of the material; for each little particle has the same composition as the larger piece from which it was obtained. With such changes we are not greatly concerned in chemistry.

3. Nature provides merely raw materials. It is evident that every material of service to civilized man must come originally from nature — from the soil, the rocks, the air. In this way we get the metals of the workshop, the drugs used in medicine, the chemicals of the laboratory, the clothes we wear, the food we eat, the furnishings of our homes. Yet very few materials as we find them in nature are suited to the needs of man advanced beyond the most primitive stage of development. From the beginning man has had to match his wits against nature to gain materials suited to his needs. At first he relied upon merely sorting out the best things he could find. He molded mud into sun-dried bricks and vessels, he pulled out the fine fibers of plant stems for his cloth, and he hammered together small flakes or grains of gold and copper, as he found them, into larger pieces. But he could not go very far in this way alone.

4. New materials from plants and animals. Pressed upon by the need of food and clothing, man very early set about to improve upon nature. When natural species of plants and animals failed to supply these necessities, he cultivated the grains and fruits and vegetables we now grow for food, and the plants that give us fibers for cloth, and improved them to such a degree that in many cases we have entirely lost track of the plants he started with. The beets of a century ago had just enough sugar in them to suggest an idea; the modern sugar beet contains as much as 20 per cent of sugar. The long-fiber cotton plant of today bears little resemblance to the natural plant from which it has been developed. So, too, with animals that supply us with meat, fat, butter, milk, eggs, and wool. They have been highly developed from natural stock.

Very little of this work has been done by chemists — most of it by the farmer of earlier times and the horticulturist and stock-breeder of more recent years. Yet it must not be overlooked that all these improvements are (in their nature) chemical changes, every plant and animal doing just what the chemist does or attempts to do in his laboratory. The raw material of nature is being more and more abundantly changed into diversified products suited to man's needs. *All living plants and animals are therefore chemical laboratories* — much more wonderful and efficient than the ones in which we work. In improving a plant or an animal, we improve some of its chemical processes that are to our own advantage.

5. New materials from lifeless matter. For the most part the chemist works with matter that is not living. He makes use of all the minerals supplied by nature, and he also employs many products of living things, such as fats, sugars, starch, and hundreds of other things. Starting with these he has produced countless new materials adapted to human needs. From the rocks he has prepared a large array of useful metals (Fig. 5) and such necessary things as lime, cement, fertilizers, pigments. From coal he has manufactured a thousand dyes, drugs, fertilizers, fuel gases, and many less familiar materials. From petroleum and wood, from the sap of trees, from milk and hides and hoofs, he has fashioned the materials that make the physical comfort and health of the poorest of today surpass the luxury of former kings.

6. The work of the chemist. There are two very different sides to the work of the chemist. He may be eager to find out the "why" of all chemical changes — why metals rust in the air; why gunpowder explodes; why some soils grow crops while others do not; why cement hardens when we wet it. Such a man wants to find out facts and then to organize his knowledge in an orderly way into a science;

he has a great desire to push out beyond the boundaries of what is already known and add to our knowledge of chemical changes.

FIG. 5. Charles Martin Hall (1863–1914)

While yet a college boy he solved the problem of cheap production of aluminum. The figure shows a statue of Hall, made of aluminum and presented to Oberlin College, where he made his first experiments and to which he left his fortune

The chemist may, however, be more interested in applying chemical knowledge to more practical problems — how to make better or cheaper steel or matches or glue, or to improve the fertility of a soil, or to make a medicine that will cure a certain disease, or to find new uses for some apparently useless thing. Most chemists are interested in both of these endeavors, and the work of each helps the other.

7. Chemical industries. Almost all the industries that transform a raw material of nature into a finished product for human use are in reality chemical industries. Such are the manufacture of soap, matches, cement, photographic materials, paint, lacquers, metals, porcelain, glass, and a host of others. All such industries depend upon the principles of chemical science, and must be supervised by someone who understands chemistry. *The industrial attainment of any* *country may be judged fairly well by the extent to which chemistry is studied in its schools and colleges.*

The chemist in charge of an industry — the industrial chemist — must supervise its processes and devise improvements. He must test the composition of each new lot of raw material that comes to his factory and modify the process accordingly. He must be able to guarantee the quality of the output of the factory so that its value may be known. He must study the possibilities of making some-

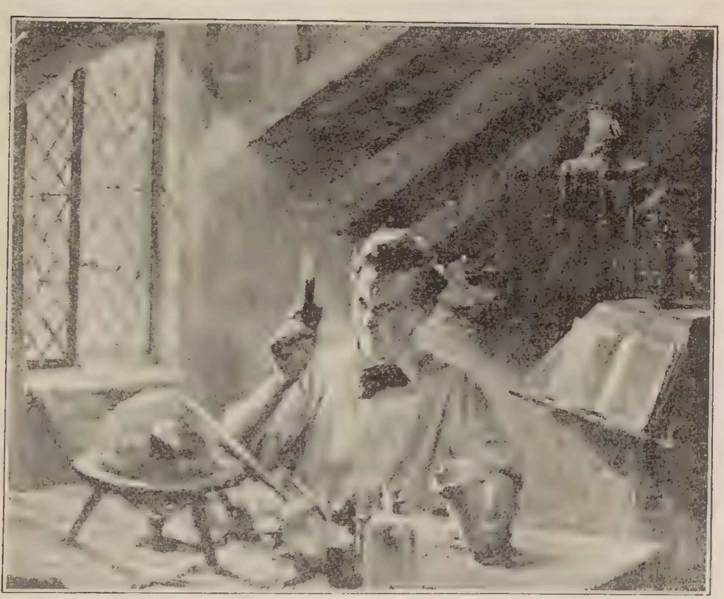

FIG. 6. William Henry Perkin — the boy who found rainbows in coal

"One Easter vacation in 1856, seventeen-year-old William Henry Perkin, a student assistant in the Royal College of Chemistry, was toiling in an improvised laboratory under the eaves of his English home. 'Throw the rubbish away,' croaked unimaginative Common Sense when the boy poured in a red fluid and got a sticky dark mass at the bottom of his test tube. 'Examine it,' whispered Science; 'it may be worth something.'" Science was right. Out of that ugly dark mud came a lovely violet-purple dye — "mauve," the first aniline dye made from coal tar. (Courtesy of Parke, Davis and Company) thing useful out of the waste material of the business. For example, from the useless tar of the gas factory he has made dyes of all colors (Fig. 6); he has taken cottonseed — formerly useless — and from it has made valuable oils, fats, soaps, and cattle food.

Since a very wide range of raw materials is employed in industry, there is almost no limit to the variety of the work of the industrial chemist. He may also help preserve health by finding out the kinds and the amounts of food best adapted to our bodies, by devising methods for purifying our water supply and for disposing of sewage, and by preparing various substances useful for fighting disease. The science of medicine depends more and more upon the chemist, who finds out the composition of those strange substances that regulate our bodies, how to make them in the laboratory, and how to prepare supplies to make up for deficiencies that sometimes cause disease.

8. Chemistry and the other sciences. Chemistry is one of the most fundamental of the sciences, for all others depend in some way upon it. The geologist and mineralogist must make chemical tests of the composition of rocks; the metallurgist and mining engineer are really industrial chemists; the zoölogist, botanist, and physician must understand the chemistry of the changes taking place in living things; one great branch of electrical engineering depends upon the production of the electric current from chemical batteries, and problems of the chemical corrosion of wires face the electrical engineer at every stage of his work. No matter what other branch of science a boy may find attractive, he must know chemistry (Fig. 7) and be able to use it.

9. Chemical knowledge incomplete. Have chemists found out all there is to know? Far from it; they have just made a good beginning. Every day sees some marked improvement in the way to make something, or a new material put to a new use. Every new invention, such as the phonograph, the moving-picture film, the radio, requires some new materials that the chemist must supply. Our knowledge of what takes place in growing plants and animals is very limited, though we are learning fast. Plants manufacture starch and cellulose chiefly from air and water, but we cannot yet do this in the most expensively equipped laboratories, nor do we have much knowledge as to how the commonest plant performs this seeming miracle. We know still less about the chemistry of our own bodies. Even in well-understood processes there is usually some detail that is not yet clear.

FIG. 7. Learning chemistry in the high school

10. The future of chemistry. There is every inducement to attract a student to chemistry as a life work. There is a wealth of problems, of vast importance to human comfort and happiness, that remain unsolved. We are rapidly using up our reserves of easily available raw material such as coal, oil, gas, wood, and metal ores, and substitutes must be found. We are exhausting our fertile lands and must learn better how to keep them productive. Every line of progress increases the number of those engaged in chemical occupation. In every progressive country the national chemical society is one of the largest of the scientific organizations. The American Chemical Society is the largest scientific society of any kind in the world, numbering over 17,000 members.

11. What is science? We have spoken of chemistry as one of the sciences. The question arises just what we mean by this word *science*. For example, is knowledge science? If so, then alchemy was a science, for the alchemists possessed a knowledge of many facts. What was lacking to make alchemy a science was the proper classification and interpretation of this knowledge so as to make it of value in the search for new facts. The discoveries that alchemists made were simply the result of chance. The chemist, on the other hand, has available a body of classified and tested knowledge to assist him in devising the experiments that will be most likely to bring the desired results. We may define science, then, as *a body of knowledge classified in such a way as to make it of value in the search for new truth.*

NOTE. *In this text the metric system of weights and measures will be used. Likewise all temperature readings will be in the centigrade system. Students not familiar with these units should refer to the table in Appendix F entitled "Relation between English and Metric Constants"; also to the discussion of thermometers given in Appendix B.*

CHAPTER SUMMARY IN QUESTION FORM

1. With what kind of changes in matter does the subject of chemistry deal?

2. What is the source of all the raw materials which civilized man uses?

3. What are the two different sides to the work of the chemist?

4. Give an instance in which the chemist has been able to utilize waste material in the manufacture of useful substances.

5. What part does the chemist play (*a*) in most industries? (*b*) in preserving the health of the people?

6. What is the relation of chemistry to other fields of study, such as agriculture, botany, physiology?

7. Name four natural products for which, eventually, substitutes must be found.

8. Enumerate some of the problems that have yet to be solved by the chemist.

9. What is meant by the word *science*?

10. Name two very important discoveries made by young men while students in college.

THOUGHT QUESTIONS

1. Give reasons for the statement that the human body is a chemical laboratory.

2. How do you account for the fact that you can get sugar from beets, and rubber from trees, but that you cannot get gold from iron?

3. What products can you name that are derived (*a*) from the sap of trees? (*b*) from milk? (*c*) from hides of animals? (*d*) from the earth?

4. Mention some of the materials and objects in your home in the preparation of which chemistry played a part.

FOR HONOR STUDENTS

1. Read and report interesting facts concerning Hall (see page 247 of "Creative Chemistry"), and Perkin (see pages 72, 73 of "Creative Chemistry").[1]

2. If there are any factories in your locality that employ chemists, select one or more of them and find out just what their chemists do.

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[1] References in this text under the heading "For Honor Students" are confined to the five books that are double-starred in the list of books given in Appendix A, and to any encyclopedia.

CHAPTER II

MATTER AND ITS KINDS

12. *Introduction.* In simple words, matter means all the stuff of which this earth, the sun, and the stars are made. We can be a little more definite by saying that *matter is anything that has weight or occupies space.* This includes not only all the solid and liquid bodies that we can see and touch, but also the various gases, many of which are invisible, such as those that make up the air we breathe.

13. Conservation of matter. Besides weight, matter has another striking characteristic; we cannot *destroy* it or *create* it. We can *change* it in many ways, but if we weigh everything we start with, and then weigh everything formed in the changes, the two weights are exactly the same. This truth is expressed in the *law of conservation of matter*, which may be stated as follows: *We are able neither to create nor to destroy matter.*

14. Forms of matter. Of course there is an infinite variety of objects having weight in the world, and we can classify these objects in a number of ways. We can say that they are all either solids, liquids, or gases. Many kinds of matter, such as water, are familiar to us in all three of these forms, ice, liquid water, and steam being the three forms of water. So we say that *the solid, liquid, and gaseous conditions are the three states of matter.*

The chemist is more interested in the *make-up* or *composition* of things than he is in their state as solids, liquids, or gases. He looks on any given specimen of matter as being either *an element, a compound, or a mixture of these.*

15. Elements. After long centuries of searching, chemists have made the remarkable discovery that all this complex world and all the infinite variety of things about us are made up of only ninety-two distinct materials, ninety of which are now known with certainty. The discovery of the two remaining ones has been announced, but as yet lacks confirmation. We think of these materials as the units or simple building materials out of which everything else is made, and we call them *elementary substances* or, more briefly, *elements*, because in combining with each other they act as units.

Many of these elementary substances, such as iron, copper, sulfur, oxygen, are well known to us; others are very rare. At ordinary temperatures most of the elements are solids (though they can be melted by heat), ten are gases, and two, mercury and bromine, are liquids. A list of all the known elements is given on the page inside of the back cover of this text.

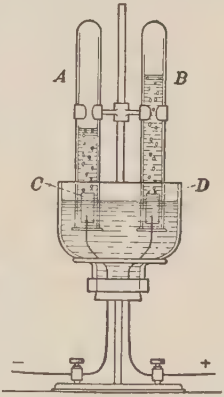


FIG. 8. Decomposition of water

When the wires shown in the figure are connected with a battery, the water in the vessel is decomposed into hydrogen, which escapes at *C* and collects in the tube *A*, and into oxygen, which escapes at *D* and collects in the tube *B*. For details see Fig. 17

16. Compounds. While there are only ninety known elements, there are hundreds of thousands of substances made up of two or more elements. Water was long regarded as an element; but if we pass an electric current through water (Fig. 8), it is broken down into two invisible gases called oxygen and hydrogen, both of which are true elements. The sugar that sweetens our food is composed of the three elements carbon, oxygen, and hydrogen. *Substances such as water and sugar, made up of two or more different elements, are called compounds.*

But compounds have a second peculiarity. *Each pure compound has a perfectly definite percentage composition.* As we shall see later on, water is made up of one part of hydrogen by weight to exactly 7.94 parts of oxygen by weight, or 11.19 per cent of hydrogen and 88.81 per cent of oxygen — never more and never less. No matter how we get the water or from what sources it comes, it has exactly this composition provided it is pure water. In a similar way sugar is made up of 42.08 per cent carbon, 6.48 per cent hydrogen, 51.44 per cent oxygen. We may now describe a pure compound in this way: *A compound is a substance made up of two or more elements in definite proportions by weight.*

17. Mixtures. The great majority of the materials we find in nature or make in factories are neither elements nor compounds, but are mixtures of elements or of compounds or of both. Many stones, such as granite, are easily seen to be made up of two or three distinct materials; and we know that salt and sand can be mixed together in any proportion, as can sugar and flour, or salt and water. Air is chiefly a mixture of the two elementary gases oxygen and nitrogen.

18. Illustration. The printed matter on this page illustrates very well the distinction between elements, compounds, and mixtures. The individual letters correspond to the elements. There are not many of them, but they can be put together in a multitude of combinations to form words. The words correspond to compounds. Each word has a definite number of letters in it and is always spelled the same way — has a definite percentage composition of letters. Both separate letters and words can be mixed in all sorts of ways to make up a great variety of sentences, corresponding to mixtures of elements, compounds, or both.

19. Substances. There are a great many things of which we often want to speak without saying whether they are elements, compounds, or mixtures. This is true of such things as paper, rubber, glass, clay, iron, sugar — all of which are well marked in character and are more or less uniform in appearance. We refer to such things as *substances.* A lamp would not be a substance, for it has many different parts; but the oil it burns is a substance, well marked in character and easily recognized by its appearance. To call it a substance would not indicate whether it is an element, a compound, or a mixture.

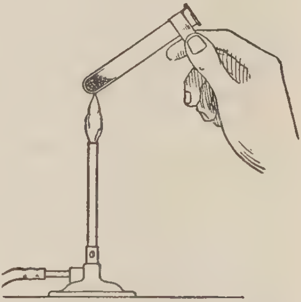


FIG. 9. The decomposition of mercuric oxide into mercury and oxygen by heat

20. Chemical changes; chemical action. If we place in a test tube one or two grams of the red solid called *mercuric oxide* and heat it (Fig. 9), we may notice some remarkable changes. The red color becomes almost black, little drops of a silver-like liquid *mercury* (often called quicksilver) appear, and finally nothing is left but the mercury. We recognize this mercury as the liquid used in thermometers and barometers, and it is very different from the red solid with which we started.

If during the heating of the red solid we have ready a long splinter of wood with a glowing spark on one end, and carefully stick this glowing end into the mouth of the test tube, the spark bursts into a flame, proving the presence of a gas in the test tube different from ordinary air. This gas is pure oxygen, which has come from the heated mercuric oxide.

In this experiment the red solid mercuric oxide has been decomposed by heat into two elements: the one a heavy silver-like liquid, the other an invisible gas. We call this decomposition a *chemical change,* and we say that a *chemical* *action* has taken place. *A chemical change may be defined as a change in the composition of matter.*

Such chemical changes are taking place all about us and in us — the burning of fuels of various sorts, the weathering of rocks (Fig. 10), the souring of milk, the changing of food into flesh and blood, the sudden blast in the quarry (Fig. 11). In all these changes, whether fast or slow, the substances resulting from chemical action differ in composition from the original materials, and nearly always in appearance as well. These changes are to be distinguished from *physical changes*, in which merely the size or shape of the object is altered — such as breaking a piece of glass, powdering a lump of coal.

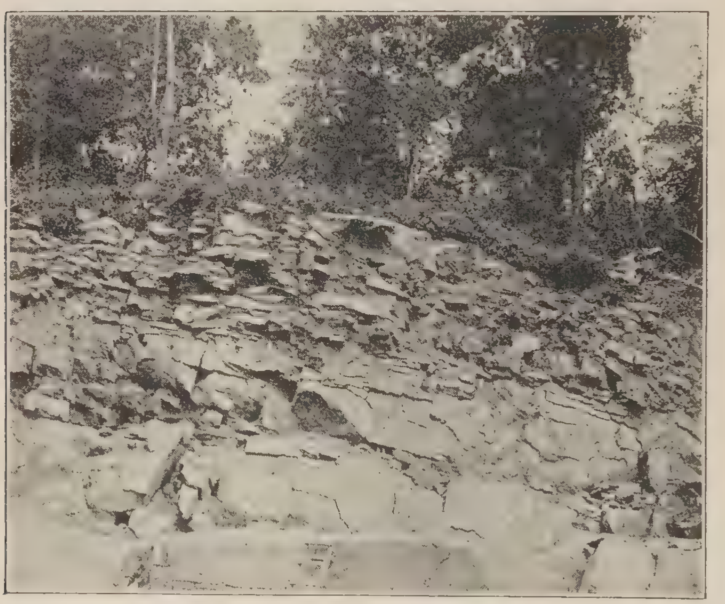


FIG. 10. A slow chemical change

Granite breaking down into small stones and soil by exposure to weathering agencies

21. Appearances not to be trusted. It is a very interesting fact that the appearance of a compound gives no clue as to what elements are present in it. Appearances are deceiving in chemistry as in many other things, and Nature is very fond of giving us puzzles. No one would guess that mercuric oxide, which looks a good deal like powdered brick, is a compound of a silvery metal and an invisible gas. It is a wonderful fact that all the water in the world is composed of two invisible gases, one of which burns with intense heat. Who would suppose that by heating sugar we could decompose it into water and black charcoal?

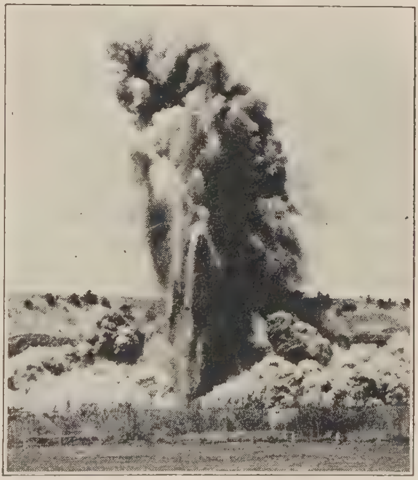


FIG. 11. A swift chemical change
The explosion of a charge in a quarry

22. Chemical affinity. When we see small pieces of iron, such as filings, attracted to a magnet, we say that some force has acted on the iron to set it in motion toward the magnet. We give a name to the force that pulls the filings to the magnet and holds them there, calling it magnetic force or *magnetism*. We notice that all objects free to move fall toward the earth when unsupported, and, arguing that there must be some force which pulls them there and holds them at the earth's surface, we call it *gravitation*.

In an entirely similar way we argue that there must be some force which causes elements to combine with each other to form compounds and which holds them together in chemical combination. We call this force *chemical* *affinity. Chemical affinity is that force which causes elements to unite and holds them in combination with each other.*

In no one of these three cases do we have a very clear idea as to the nature of the force or how it acts; but we know the force exists because of the effects we see. We give it a name so that we can talk about it.

23. Relative abundance of the elements. There are ninety known elements, and it would be natural to suppose that they are equally abundant on the earth. This is far from the fact. It is very unexpected to find that one of them, oxygen, makes up nearly half the weight of all the part of the world of which we have any knowledge — the atmosphere, water, the surface rocks, and all living things. Yet oxygen was not discovered until about one hundred and fifty years ago. A second element, silicon, constitutes more than one fourth of the solid earth as we know it, so that two elements together compose about three fourths of the world known to us. Of course we know very little about the composition of the earth below the surface rocks.

Professor F. W. Clarke, of the United States Geological Survey, has made the following estimate of the elements in the solid part of the earth's crust (exclusive of water):

COMPOSITION OF THE EARTH'S CRUST

	Per Cent		Per Cent
Oxygen	46.71	Sodium	2.75
Silicon	27.69	Potassium	2.58
Aluminum	8.07	Magnesium	2.08
Iron	5.05	Hydrogen	0.14
Calcium	3.65	Other elements	1.28

Fortunately it is not necessary to study more than one third of the elements to gain a very good knowledge of chemistry.

24. The number of compounds. The number of definite compounds that have been described and can be made when desired is more than half a million, and each year many more are added to the list. But in learning the principles of chemistry it is not necessary to become familiar with any large number of these compounds.

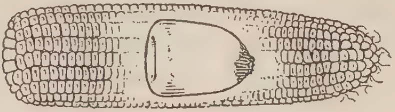


FIG. 12. Elements in a kernel of corn

Each kernel of corn has the composition: oxygen, 46 per cent; carbon, 45 per cent; hydrogen, 6 per cent; nitrogen, 2 per cent; mineral matter, 1 per cent

25. Elements in living things. Relatively few of the elements appear to be essential to life. The four elements carbon, oxygen, hydrogen, and nitrogen make up about 99 per cent of a kernel of corn (Fig. 12). The table below, compiled by Professor Sherman, an authority on the chemistry of living things, gives the average composition of the human body. Apparently these are the only elements which living things require, though traces of others may be necessary.

AVERAGE COMPOSITION OF THE HUMAN BODY

	Per Cent		Per Cent
Oxygen	65.00	Sodium	0.15
Carbon	18.00	Chlorine	0.15
Hydrogen	10.00	Magnesium	0.05
Nitrogen	3.00	Iron	0.004
Calcium	1.50	Iodine	0.00004
Phosphorus	1.00	Fluorine Silicon and other elements	traces
Potassium	0.35		
Sulfur	0.25		

26. Occurrence of the elements. Most of the elements occur in nature in combination with other elements, or *in the combined state*; for example, calcium is found in combination with carbon and oxygen as marble or limestone. The elements present in our bodies are all in the form of compounds, of which water is the most abundant.

When an element is found in nature uncombined with another element, as is often the case with oxygen or gold or sulfur, we say it occurs *in the free state* or *native.*

27. Names of the elements. The names given to the elements have been selected in a great many ways, the one who discovers an element having the right to give it a name. Some names, such as iron and gold, are very old, and we are not sure of their original meaning. Many names refer to some striking property of the element. For example, the name *bromine* means "bad smell," referring to the extremely unpleasant odor of the substance. Other elements have been named for countries, as *germanium* and *columbium*; or for god or hero of old, as *thorium* and *tantalum.*

28. Symbols. Just as we indicate the names of states by such abbreviations as Pa., Mo., O., so the chemist uses abbreviations called *symbols* for the names of elements. Sometimes merely the first letter of the name of the element is used: C for carbon, O for oxygen, N for nitrogen. Usually (as with states) it is necessary to add a second letter to the symbol because several names begin with the same letter. Thus C stands for carbon, Ca for calcium, Cl for chlorine, and Cd for cadmium. Some symbols are abbreviations of the old Latin name for the element. In this way Fe (*ferrum*) stands for iron, Cu (*cuprum*) for copper, and Hg (*hydrargyrum*) for mercury. The symbols for all the elements will be found in a list on the inside of the back cover.

29. The symbol and the atom. As the result of a great many experiments we now know that any given quantity of an element is made up of a vast number of tiny particles called *atoms*, much as a load of very pure sand is made up of nearly uniform grains, although the grains of sand are far larger than the atoms of elements. Now the chemist finds it convenient to make the symbol of an element stand for *one atom* of that element. Thus H stands for one atom of hydrogen, O for one atom of oxygen, and Hg for one atom of mercury.

30. How the chemist uses symbols. Since every compound contains at least two elements, it must also contain at least two kinds of atoms, each having its own symbol. In a kind of chemical shorthand the chemist uses the symbols of the atoms in a compound to show its composition, instead of spelling out each name. Thus mercuric oxide contains mercury atoms and oxygen atoms; and the chemist has found out that they are present *in equal numbers.* Accordingly, in chemical shorthand the name "mercuric oxide" is written HgO, which means a compound of mercury and oxygen with atoms of each in equal numbers — one to one. The shorthand chemical name, HgO, is called the *formula* of the compound.

When experiment has shown that mercuric oxide is decomposed by heat into mercury and oxygen, the chemist expresses this fact in the form of an *equation,* as follows:

$$HgO \longrightarrow Hg + O$$

This equation represents the name of the compound decomposed and of the elements formed from it.

Similarly it has been found by experiment that water is made up of oxygen and hydrogen, and that it contains two atoms of hydrogen for every atom of oxygen. The formula of water is therefore written H_2O, the subscript figure 2 referring to the symbol H just before it. This is the same as though it were spelled out: H-two O.

As we go along we shall see how the chemist finds out how many of each kind of atoms there are in a given chemical compound, and we shall also see that he puts many more facts into these shorthand formulas and equations than have been explained here. At present we shall use them merely to indicate the relative number of atoms in different compounds, and what compounds are decomposed or formed in chemical actions.

31. Physical properties and chemical conduct. In getting acquainted with any given element or compound, we shall want to know (1) what it is like and (2) how it acts toward other things; in other words, its *physical properties* and its *chemical conduct.*

32. Physical properties. The physical properties of a substance are what it is like, meaning by this its physical state (whether it is a solid, a liquid, or a gas), its color, odor, taste, melting point, boiling point, weight or density, hardness, solubility, and any other marks by which we can describe it.

33. Chemical conduct. By the chemical conduct of a substance we mean how it acts toward other substances, or how readily it is decomposed by heat, or by the electric current, or by sunlight — in general, how it behaves chemically.

34. Energy. The chemist is not only concerned with *matter*, but he is equally interested in *energy*. Everyone knows that when coal burns heat is given out, that under proper conditions an electric current passes along a wire, and that by means of the steam engine and the motor both the heat and the electric current can *be made to do work.* Anything that can do work is said to *possess energy,* and *we may define energy as the ability to do work.* Heat, the electric current, light, movement of bodies, magnetism, are forms of energy.

35. Chemical energy. Since a great deal of heat is often given out when two substances combine, we argue that these substances must have possessed energy of some kind, and we call this *chemical energy.* In a battery the chemical energy is changed into electrical energy as well as into heat. The chemist is especially concerned with this form of energy.

36. Conservation of energy. Just as we cannot create or destroy matter, so *we cannot create energy out of anything* *except some other form of energy, nor can we destroy it.* This statement is called the *law of conservation of energy.* We can change one form of energy into another, as when we change heat into electrical energy by means of a steam engine and a dynamo, or electrical energy into heat and light in the electric lamp (Fig. 13); but we cannot destroy or create it.

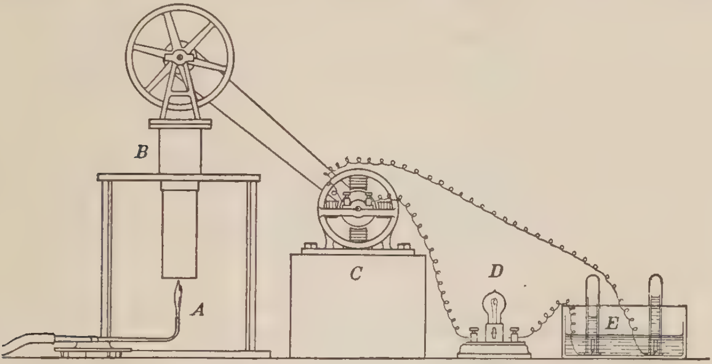


FIG. 13. Transformations of energy

The heat of the flame *A* is changed into energy of motion in the engine *B* and this into electrical energy in the dynamo *C*. The electrical energy is changed into light in the lamp *D* and into chemical energy in the cell *E*

CHAPTER SUMMARY IN QUESTION FORM

1. "The world is made up of matter." What is meant by the word *matter* in this sentence?

2. (*a*) What is the name of the law that expresses our belief regarding the creation and destruction of matter? (*b*) State the law.

3. (*a*) Give two ways in which we may classify matter. (*b*) In which of these is the chemist more interested?

4. (*a*) What is an element? (*b*) How many are known? (*c*) How many remain to be discovered?

5. (*a*) Name two characteristics of compounds. (*b*) How many compounds are known?

6. How do mixtures differ from elements and compounds?

7. (*a*) Distinguish between *physical changes* and *chemical changes.* (*b*) Give an example of each.

8. Give an example to illustrate the meaning of the term *chemical action.*

9. (*a*) Can you tell by its appearance what elements are in a compound? (*b*) Give an example to illustrate your answer.

10. What do we call the force that causes elements to unite to form compounds?

11. Name two elements that together make up about three fourths of the earth's crust.

12. Name three elements that constitute over 90 per cent of our bodies.

13. Gold occurs in nature in a *free state*, iron in a *combined state.* Explain the meaning of this statement.

14. Give, and illustrate by example, three ways in which elements have received their names.

15. (*a*) What is the symbol of an element? (*b*) How are symbols derived?

16. (*a*) What is the difference between a symbol and a formula? (*b*) Show by an example how the chemist expresses a chemical change by the use of symbols and formulas.

17. What questions are to be answered under the headings (*a*) "Physical properties of an element" and (*b*) "Chemical conduct of an element"?

18. (*a*) What is the difference between matter and energy? (*b*) Name different forms of energy. (*c*) What kind of energy does a storage battery possess?

19. (*a*) In what respect are matter and energy alike? (*b*) State the law of each that expresses this similarity.

THOUGHT QUESTIONS

1. Explain the phrase "definite percentage composition."

2. Air is composed largely of a mixture of oxygen and nitrogen. Suppose it were a compound of these two elements; in what respects do you think it might differ from the mixture?

3. Select from the words in column *A* the one (or ones) that most accurately describe each of the words under *B*.

A

Element
Compound
Mixture
Substance
None of the above

B

Water
Sugar
Grapefruit
Coffee
Cream
Lead
Salt
Gold
Butter
Copper

4. Suppose a certain substance is not changed on heating. Does this prove the substance to be an element?

5. We say that matter cannot be destroyed, but we also say that a candle burns up. Can you account for the disappearance of the candle?

6. Account for the fact that the ancients were familiar with gold but not with aluminum, which is far more abundant.

7. What form of energy is used to bring about the chemical change that takes place in (*a*) the lighting of a match? (*b*) the taking of a photograph? (*c*) the charging of a storage battery?

8. State some transformations of energy that take place in (*a*) the running of an automobile; (*b*) the riding of a bicycle.

9. The energy of the falling water at Niagara Falls is utilized for propelling, heating, and lighting the street cars in Buffalo. Give the transformations of energy involved.

FOR HONOR STUDENTS

1. Weigh out a piece of fine iron wire equal to the weight of iron in your body. Does the fact that the percentage of iron in the body is so small signify that it is unnecessary to the health of the body?

2. In a general way, how would one proceed to tell whether any given substance is an element, a compound, or a mixture?

3. Give the source of (*a*) the heat in your body; (*b*) the heat generated in an electric light; (*c*) the heat given off by a burning candle; (*d*) the heat generated in pumping air into an automobile tire; (*e*) the heat generated by sawing a piece of hard wood.

CHAPTER III

OXYGEN

The Most Abundant of All the Elements

37. *Introduction.* About two hundred years ago there was born in England a boy whose name, Joseph Priestley, is now familiar to every chemist. Young Priestley studied for the ministry, and at the age of twenty-two began to preach. Some of the people were not pleased with his religious and political views, however, and finally they showed their displeasure by burning his church and his house. As a result of such treatment Priestley came to America (1794) and settled in Northumberland, a little town in Pennsylvania, where he spent the remainder of his life.

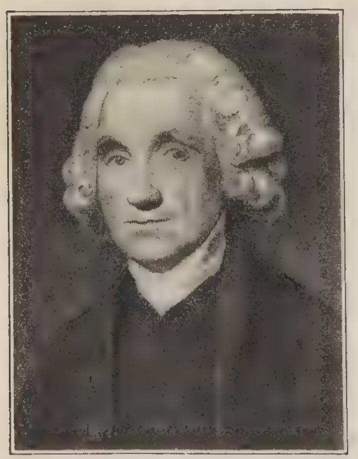


FIG. 14. Joseph Priestley (1733–1804)

The discoverer of oxygen

But Priestley (Fig. 14) was not only a minister; he was by nature a true scientist. He had an inquiring mind, keen powers of observation, and a great desire to know the truth about all things. He liked to experiment, especially with gases, or "airs" as he called them, and it is chiefly because of his discovery of six or eight important gases and his study of their properties that we remember him. One day (August 1, 1774), while trying the effect of heat upon a number of solids, he put a small amount of mercuric oxide (§ 20) into a tube, filled it with mercury, and then inverted the tube in a vessel of mercury as shown in Fig. 15. The oxide, being lighter than the liquid mercury, rose to the top of the tube. Priestley then heated this oxide by focusing the sun's rays upon it with a large glass lens. He soon found that a gas was evolved which collected in the top of the tube. This was a surprise, but he wrote: "What surprised me more than I can well express was that a candle burned in this air with a remarkably brilliant flame." "This air" was none other than the gas we now call *oxygen*, and Priestley's discovery of it must be regarded as one of the greatest in the history of chemistry; for it led the great French chemist Lavoisier (Fig. 20) to find out just what takes place when substances burn.

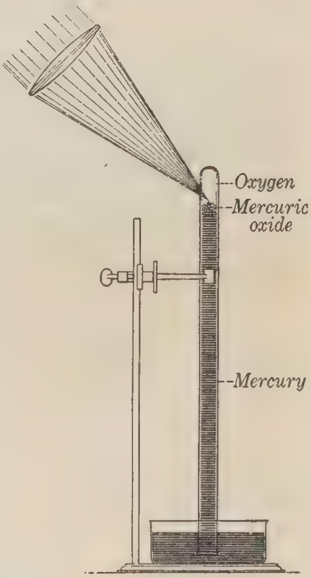


FIG. 15. Priestley's method of preparing oxygen by heating mercuric oxide

38. Where does oxygen occur? Oxygen is in us and all about us. The atmosphere is the great storehouse of free oxygen. If we were to separate 100 liters of dry air into its constituents, we should have about 21 liters of oxygen, 78 liters of nitrogen, and 1 liter of other gases. Combined with other elements, oxygen forms eight ninths, by weight, of water; nearly half of the rocks constituting the earth's crust; and over half of all plants and animals.

39. Preparation. While oxygen occurs so abundantly in nature, it is always either mixed with other gases, as in the air, or combined with other elements as compounds. For many purposes, however, we must have the pure gas. Just how to obtain it free from all other substances is therefore an important problem. Since it is so abundant in the air, and air costs nothing, we should naturally try to obtain it from this source. The separation of oxygen from the other gases with which it is mixed in the air is, however, a difficult matter requiring expensive machinery, so that this method (which will be described later) is used only when large quantities of the gas are desired for commercial purposes (Fig. 16). In the laboratory, where only small amounts are needed for a study of the properties of the element, oxygen is most conveniently prepared by decomposing certain of its compounds. The compounds best adapted for this purpose are (1) mercuric oxide, (2) water, and (3) potassium chlorate.

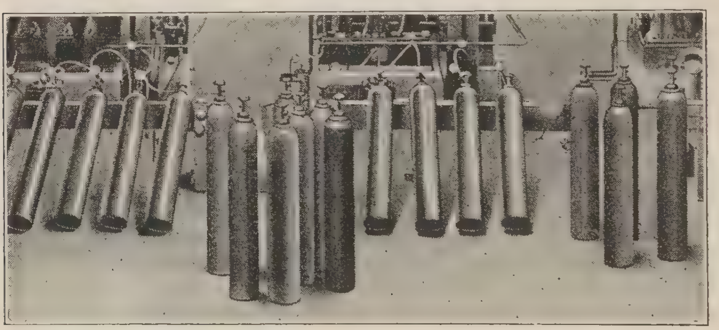


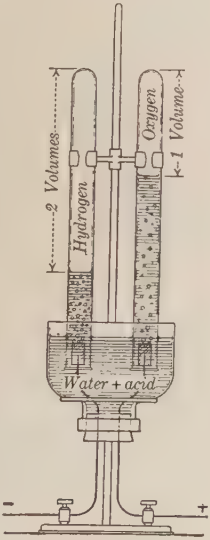
FIG. 16. Commercial oxygen in steel containers

1. *Preparation from mercuric oxide.* This method is too expensive for ordinary use, but it is of interest because it is the one that led Priestley to discover oxygen. Mercuric oxide is a compound consisting of 7.4 per cent of oxygen and 92.6 per cent of mercury. When heated, this compound,

as we have learned (§ 37), decomposes into mercury and oxygen, and we may represent this change as follows:

$$HgO \longrightarrow Hg + O$$

2. ***Preparation from water.*** As we have learned (§ 16), water is a compound containing 88.81 per cent oxygen and 11.19 per cent hydrogen by weight. It is very difficult to separate it into its elements by heat, but it can be decomposed easily by the use of electrical energy as shown in Fig. 17.



Two tubes entirely filled with water containing a few drops of sulfuric acid are inverted in a vessel of the same liquid, as shown in the figure. Into the mouth of each tube extends a piece of platinum foil attached to a wire. These wires are connected with a battery supplying from 6 to 10 volts. The electric current flows from one wire to the other through the water. The water is decomposed by the current into oxygen, which escapes from one of the pieces of platinum, and hydrogen, which escapes from the other. The gases, being much lighter than water, rise in the tubes and are collected as shown in the figure

FIG. 17. Apparatus for preparing oxygen (and hydrogen) by decomposing water by the electric current

Since the formula of water is H_2O (§ 30), we may represent the reaction that takes place when water is decomposed in the following shorthand way:

$$H_2O \longrightarrow 2\ H + O$$

It is important to note that this method serves for the preparation of hydrogen (which we shall study in the following chapter) as well as of oxygen; also that *for each volume of oxygen set free, we obtain two volumes of hydrogen.* This latter fact is of great importance, and we shall refer to it many times in later chapters.

3. ***Preparation from potassium chlorate.*** This is the usual method employed in the laboratory. Potassium chlorate is a white solid compound of potassium, chlorine, and oxygen. Its formula is $KClO_3$, and it contains 39.2 per cent of oxygen. When it is heated above its melting point the oxygen is all set free (Fig. 18), leaving a white solid compound of potassium and chlorine called potassium chloride (KCl). The change may be represented as follows:

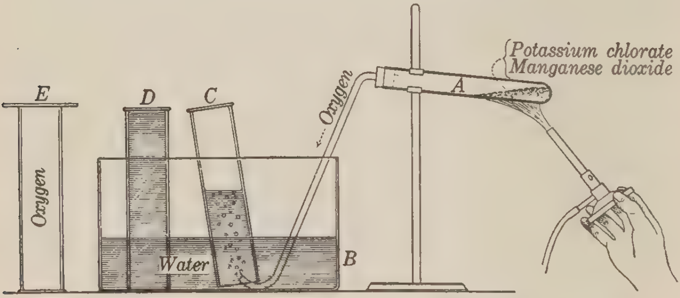


FIG. 18. The preparation of oxygen from potassium chlorate

The chlorate is first mixed with a little manganese dioxide, and the mixture transferred to the tube *A* and gently heated. The oxygen in the potassium chlorate is evolved and escapes through the exit tube. It is collected by bringing over the end of the tube a cylinder *C* completely filled with water. The gas rises in the cylinder and displaces the water

$$KClO_3 \longrightarrow KCl + 3\,O$$

40. Catalytic agents. In preparing oxygen from potassium chlorate we generally mix with the chlorate, before heating it, a little manganese dioxide (a black solid compound of manganese and oxygen). The potassium chlorate gives up its oxygen more rapidly and evenly when the manganese dioxide is present. Why does the manganese dioxide have this effect? It may be said at once that we do not know. Apparently it undergoes no change in itself. Certainly it gives up no oxygen, for the weight of oxygen obtained is always 39.2 per cent of the chlorate used, whether or not the manganese dioxide is present. Just as the mere presence of a teacher in the study room may increase the amount of studying done, so the mere presence of the manganese dioxide, in some way, causes the chlorate to give up its oxygen more readily. *This is but one example of many in which the rate of change in a reaction is influenced by the mere presence of an apparently unchanged substance.* Such substances are called *catalytic agents*, or *catalysts*. A great many chemical processes depend upon suitable catalysts for their success.

41. Physical properties. Oxygen is a colorless gas without taste or odor. It is slightly heavier than air. (For weight of 1 liter of various gases, see table facing back cover.) It is very slightly soluble in water, 100 volumes of water dissolving only about 4 volumes of the gas under usual laboratory conditions of temperature and pressure.

42. Chemical conduct. While oxygen acts on most substances at ordinary temperatures, the action may have to continue for days or even weeks before the change can be detected, as in the rusting of iron. At higher temperatures, however, it becomes very active. Thus, if we place a splint of wood in a tube of oxygen, no apparent change takes place; but if we light the end of the splint and extinguish the flame so as to leave a glowing coal, and then bring it into the tube, the coal bursts

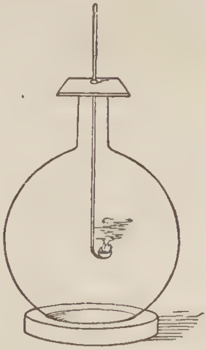


FIG. 19. Burning sulfur in oxygen

into a flame, and the splint burns rapidly. Sulfur burns in air with a very little flame; in oxygen the flame is increased in size and brilliancy (Fig. 19). Substances that burn in air only with great difficulty, such as iron, burn readily in oxygen; others, such as phosphorus, burn readily in air but burn in oxygen with dazzling brilliancy.

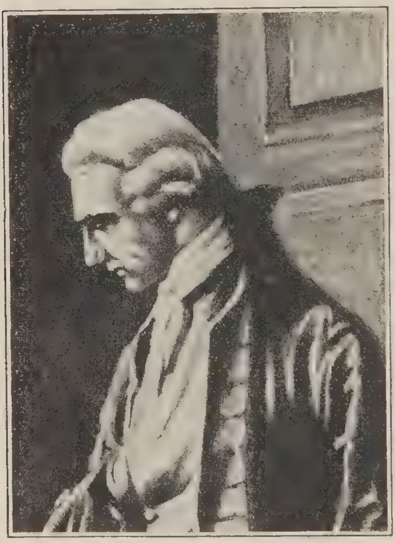


FIG. 20. Antoine Laurent Lavoisier (1743–1794)

Distinguished French chemist, one of the greatest in the history of chemistry. He overthrew the phlogiston theory by his demonstration of the true nature of combustion. He was guillotined during the French Revolution because of his connection with the government

43. Fire. What changes take place when a substance burns? We are so accustomed to fire that we rarely stop to think that there must have been a time when it was unknown. The ancients believed that in the beginning man was without fire but that Prometheus stole some from the chariot of the sun and brought it to earth. The discovery of fire, together with the means of producing it, must be regarded as one of the great discoveries. The fact that the burning substance gave out light and heat naturally attracted attention, and many ideas were advanced to explain this fact. The phlogiston theory (see Introductory Chapter, p. 6) was the first serious attempt to account for fire. After Priestley discovered oxygen, Lavoisier concluded that since substances burn so readily in oxygen, this gas must have something to do with burning.

44. Heating of metals in air. In place of merely speculating about fire, Lavoisier (Fig. 20) put his views to the test of experiments, which is the only way to find out the facts. He soon found that when metals are burned in a closed vessel filled with air or oxygen they increase in weight, and that at the same time a certain amount of the oxygen present disappears. Moreover, he found that the increase in the weight of the metal in burning was equal to the weight of the oxygen that disappeared. He therefore came to the conclusion that *when a metal, or indeed any element, burns, it combines with oxygen, and the product formed is a compound of the element and oxygen.* This discovery of Lavoisier, which led to the true explanation of burning, is regarded as one of the greatest of all discoveries in chemistry.

Not only do many of the elements burn in oxygen, but many compounds also burn in this gas. In such cases, as a rule, the compound is decomposed, and each of the elements present combines with the oxygen. Sometimes the compound unites with oxygen without being decomposed.

45. Changes in weight accompanying burning. That the product formed when a metal burns weighs more than the original metal is easily shown as follows: Some very fine iron powder is placed in a small porcelain dish *A* and the dish counterpoised on a balance, as shown in Fig. 21. The dish is then removed from the balance and gently heated until the iron begins to burn. After the glowing ceases and the dish is cool, the dish is returned to the balance. The pan on which the dish *A* rests at once sinks (Fig. 22), showing an increase in weight.

If Lavoisier's explanation (§ 44) is correct, then the product formed when a metal or any substance burns ought to weigh more than the substance burned. The question will naturally arise whether this is true in case of a candle; for the candle entirely disappears on burning. A little reflection, however, suggests that perhaps the products formed when the candle burns may be invisible gases which escape unnoticed into the air. That this is the case and that these gases weigh more than the candle is easily shown as follows: A wide glass tube or lamp chimney *B* (Fig. 23) is loosely filled with pieces of caustic potash, a compound that readily absorbs the gases formed when the candle burns. The tube and contents are suspended above a candle *A*, as shown in the figure, and the whole apparatus counterpoised by weights *C*. The candle is then lighted. The hot gaseous products formed on burning rise in the tube and are absorbed by the caustic potash. As the candle burns, the pan upon which it rests gradually sinks, showing the increase in weight caused by the union of the oxygen in the air with the elements of the candle when it burns.

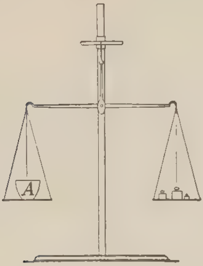


FIG. 21. A porcelain dish *A* containing very fine iron powder counterpoised on a balance

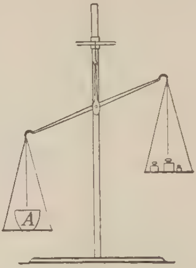


FIG. 22. After being heated in the air, the contents of the dish *A* are heavier than before

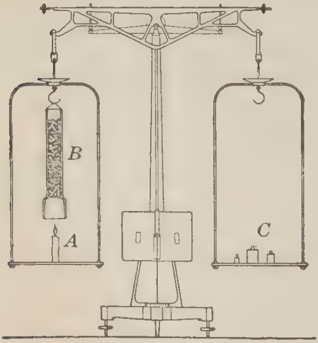


FIG. 23. Experiment to show that invisible gases are formed when a candle burns and that these gases weigh more than the burned part of the candle

46. Oxidation; burning; combustion. When a substance combines with oxygen we say that the substance is *oxidized* or that it undergoes *oxidation.* If the change takes place slowly no light is given off, and unless careful measurements are made no heat is noticed. The decay of vegetable matter, such as wood and leaves, and the rusting of metals are examples of this slow oxidation. But if the change takes place very rapidly, so much heat may be evolved as to cause the substance undergoing oxidation to glow or to burst into a flame, and we say that the substance *burns* or undergoes *combustion.* The word "combustion" is not limited to those changes in which oxygen is taking part, but is used when *any two substances* combine rapidly and give off light. These statements may be summed up as follows: *"Oxidation" is the word applied to the change that takes place when any substance combines with oxygen. The word "combustion" is applied to the change that takes place when any two substances combine rapidly and give off light.*

47. Oxides; products of oxidation. We have seen that when an element burns in oxygen, a compound of the element with oxygen is formed. Such compounds are called *oxides.* Thus, iron on burning forms oxide of iron, and sulfur forms oxide of sulfur. A candle is composed chiefly of compounds of carbon and hydrogen. When it burns the carbon unites with oxygen to form an oxide of carbon known as carbon dioxide, and the hydrogen unites with oxygen to form water, which is an oxide of hydrogen. All but about half a dozen elements form oxides, and many of them form more than one, so that a large number of these compounds are known. Some are solid bodies, as in the case of oxides of mercury and iron; others are liquids, water being the most familiar example; quite a number are gases, as is true of the oxides of carbon and of sulfur.

The oxides formed when any substance undergoes oxidation are known as the *products of oxidation* of that substance. Thus, oxide of iron is the product of combustion of iron, while carbon dioxide and water are the products of combustion of the candle.

To sum up these facts we may say, then, that *an oxide is a compound formed by the union of any one element with oxygen. The particular oxides formed when a substance undergoes oxidation are known as the products of oxidation of that substance.*

48. Rapidity (or speed) of combustion. We all know that the same substance may burn with different degrees of rapidity. It is important to know how the rapidity, or speed, of the combustion can be increased or decreased. A number of factors may affect the speed, but the two most important are the following:

1. ***Temperature.*** Everyone knows that a lump of coal thrown into a hot furnace will burn faster than if placed on burning kindling wood in the same furnace. This is owing to the fact that the hot furnace increases the temperature of the coal, and this increase in temperature causes a corresponding increase in combustion. Within certain limits it may be stated in general terms that *combustion takes place more rapidly the higher the temperature.* Oxidations which may require years for completion at a low temperature may take place in a few seconds at a very high temperature.

2. ***Surface exposed.*** Since ordinary combustion is due to the union of one or more elements with oxygen, it follows that the more oxygen can be brought into contact with the substance undergoing combustion, the more rapidly the combination should take place. This can be done by increasing the extent of the surface of the substance undergoing combustion. A log of wood burns slowly. Cut the log into pieces, and the speed of combustion increases because oxygen comes into contact with the wood not only over the old surface of the log but over the new surfaces made by the splitting. Split the pieces into fine splinters and the

speed of combustion is still further increased. Grind the splinters into fine dust and float these in the air so that each little particle is surrounded by the oxygen in the air, and combustion, if started, will take place so rapidly as to be nearly instantaneous, producing a violent explosion. In this way we account for the explosions of flour mills and starch factories, the air of which often contains large quantities of combustible dust (Fig. 24).

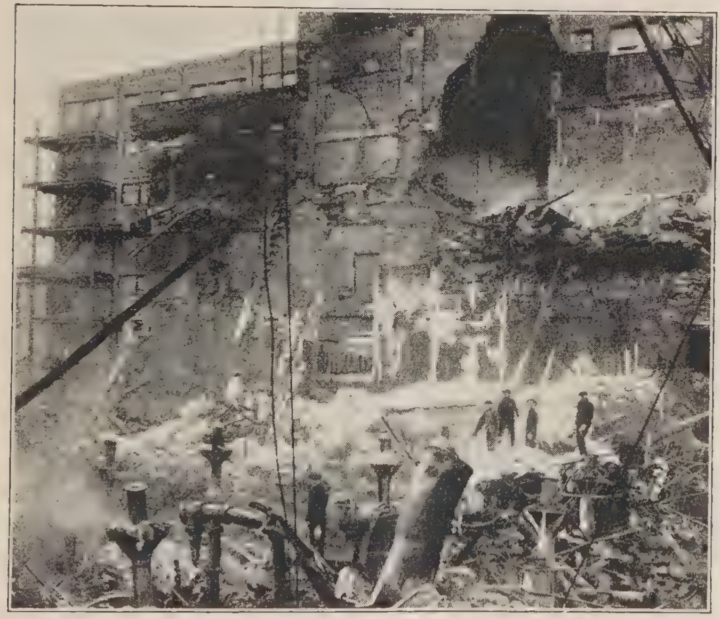


FIG. 24. Results of an explosion of starch dust in which forty-two men were killed and a large number seriously injured. (Courtesy of the United States Bureau of Mines)

49. Heat of oxidation and combustion. Evidently a given substance may either undergo a slow oxidation or undergo combustion. Thus a piece of phosphorus exposed to the air in a cold room slowly wastes away until it has all disappeared into smoke consisting of an oxide of phosphorus, but if it is touched with a lighted match it takes fire and burns very rapidly, giving out much heat. The product is the same in both cases, namely, oxide of phosphorus. *Apparently* the difference lies in the amount of heat given off, but very accurate experiments demonstrate that this too is *exactly the same.* In the one case the action is so slow that the heat is conducted away as fast as it is liberated, and escapes notice; in the other it is given off so rapidly as to be very striking. A similar relation has been found to hold true in all cases of combustion. *The heat given off in oxidation is exactly the same whether the action is fast or slow, provided the same compound is formed.*

50. Spontaneous combustion. We have seen that heat is given off when a substance oxidizes and that the rate of oxidation increases with the temperature. Consequently, if the conditions surrounding oxidation are such that the heat given off cannot escape, the temperature will steadily rise, and because of this the rate of oxidation will increase. The increased heat thus set free will still further raise the temperature until the oxidation passes into active combustion, the point at which this occurs being called the *kindling temperature.* Materials taking fire in this way are said to undergo *spontaneous combustion.* Linseed oil, used in paints, undergoes rather rapid oxidation in air, and oily rags left by painters not infrequently occasion disastrous fires.

51. Importance of oxygen. Oxygen is one of the most important of the elements. If it were suddenly withdrawn from the air, all human life would become extinct in a few minutes. Indeed, oxygen is essential to all life, both animal and vegetable, except some low forms of plant life. It is also a great purifying agent, for in the presence of certain minute bacteria, which in some way assist in the process, the oxygen in the air acts upon the dead products of animal and vegetable life and converts them into harmless substances. For example, in sewage-disposal plants, sewage is forced into the atmosphere in fine sprays (Fig. 25) so that the oxygen can come in contact with the putrid matter in the sewage, thus purifying the sewage and preventing it from becoming a menace to health. The water supplied to New York City is likewise sprayed in the air to assist in its purification.

The greatest use of *pure* oxygen is for obtaining high temperatures, making it possible not only to cut into pieces large metal plates but also to weld metals together, as will be explained later. Enormous quantities of the gas are prepared annually from air for this purpose. Smaller quantities are used for burning out the carbon deposited in the cylinders of motor-car engines, for preparing certain compounds of oxygen, and for the treatment of diseases, such as pneumonia. Aviators are always supplied with the pure gas for use at high altitudes (Fig. 26), and miners use it for rescue work in mines after explosions.

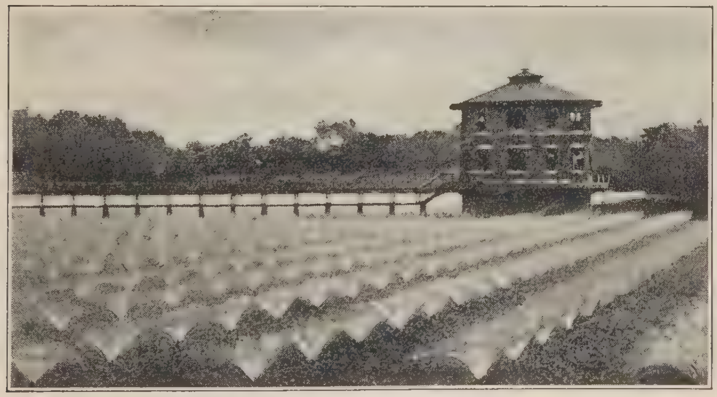


FIG. 25. Sewage-disposal plant at Columbus, Ohio, in which the sewage is sprayed into the air to secure its oxidation

52. Variation in volumes of gases. Facing the back cover of this text will be found a table giving the weight in grams of 1 liter of each of a number of common gases. It is well known that the volume of a gas varies with the temperature of the gas as well as the pressure to which the gas is subjected. If we are to be exact, then, in giving the weight of 1 liter of a gas, we must specify the conditions of temperature and pressure under which the gas is measured. This matter will be described in more detail in Chapter V. In the meanwhile it will be understood, in all references to weights of definite volumes of gases, that the volumes have been measured at a temperature of zero and a pressure equal to the average normal pressure of the atmosphere at the sea level.

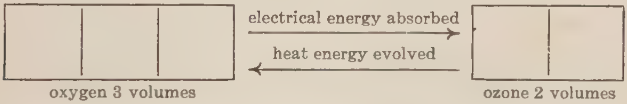
FIG. 26. The oxygen gas helmet

The photograph shows Lieut. John A. Macready, fitted with a supply of oxygen, about to attempt an altitude record at the Wright Field, Dayton, Ohio. He reached an altitude of 37,569 ft. — at that time the world record

Ozone

53. General. Everyone who has worked with an electrical machine by which sparks of electricity are generated has noticed the peculiar odor we associate with such machines. What is the cause of this odor? Many ideas have been advanced to account for it, but we now know that the odor is that of a new gas formed by the action of the electrical discharge on the oxygen present in the air. We call this gas *ozone*, the word being derived from the Greek word meaning "odor."

54. Preparation and properties. To prepare ozone it is only necessary to pass an electrical discharge through pure oxygen or air. The ozone formed easily changes back into the oxygen from which it was formed. As the preparation proceeds, the amount of ozone reverting to oxygen soon equals the amount of oxygen changed into ozone. We then say that the oxygen and ozone *are in equilibrium with each other*. Usually this equilibrium is reached when about 5 per cent of the oxygen exposed to the action of the electrical discharge has been converted into ozone. During the change of oxygen into ozone there is a reduction in volume, three volumes of oxygen forming but two volumes of ozone. These facts may be represented as follows:



It is possible to prepare pure ozone, but the process is very difficult and dangerous, since pure ozone has a tendency to change back into oxygen with explosive violence.

At ordinary temperatures ozone is a pale blue gas 1.5 times as heavy as oxygen. It is a very powerful oxidizing agent — much more so than oxygen itself. Although it is so active, but little use is made of it.

55. Relation between oxygen and ozone. Just how can we account for the change of oxygen into ozone, and how do these two substances differ in composition? At first we might think that the oxygen, when acted upon by the electric discharge, combines with some other element, and that the ozone formed is an oxide of that element; but this cannot be true, for ozone can be formed from pure oxygen alone. We now know that the change of oxygen into ozone is one of energy as well as of matter. When the electric discharge is passed through the oxygen, some of the electrical energy is stored up in the oxygen in the form of chemical energy, and it is because of this increase in energy that the oxygen acquires new properties; in other words, it becomes a new substance.

56. Allotropic forms of matter. Just as oxygen and ozone are the same kind of matter, so we shall find that many of the other elements occur in forms differing greatly in properties, this difference being due to their different amounts of chemical energy. Such forms of matter are known as *allotropic forms.*

CHAPTER SUMMARY IN QUESTION FORM

NOTE. The usual abbreviations for units of weight and volume will be used, such as g. for grams, kg. for kilograms, cc. for cubic centimeters, lb. for pounds, cu. ft. for cubic feet.

1. When and by whom was oxygen discovered?

2. (*a*) From what compound was oxygen first obtained? (*b*) Through what agency was the oxygen liberated from this compound?

3. (*a*) Where do we find oxygen in the free state? (*b*) in the combined state?

4. Explain how you can obtain oxygen from (*a*) mercuric oxide; (*b*) water; (*c*) potassium chlorate.

5. What is the source of the oxygen sold on the market?

6. In the laboratory method for obtaining oxygen, does the oxygen obtained come from the potassium chlorate or the manganese dioxide or both?

7. What name do we give to a substance that aids chemical action, yet remains unchanged at the end of the action?

8. (*a*) What questions do we answer in giving the physical properties of an element? (*b*) Answer these questions in reference to oxygen.

9. (*a*) What do we mean when we say that an element such as iron is oxidized? (*b*) What name do we give to the product formed?

10. What changes take place when an element such as sulfur or iron burns?

11. (*a*) How did the alchemists explain burning? (See Phlogiston, p. 6.) (*b*) Who first gave the true explanation of burning?

12. Matter cannot be destroyed, yet a candle entirely disappears on burning. Explain.

13. How does the weight of a candle compare with the weight of the products formed when it burns?

14. Mention two ways by which you can make a substance burn more rapidly.

15. Does it make any difference in the amount of heat developed whether a substance burns slowly or rapidly?

16. (*a*) What kind of combustion is said to occur when a substance takes fire without the application of external heat? (*b*) How do you account for such fires?

17. Give three uses of oxygen.

18. How could you test for pure oxygen?

19. Explain the meaning of each of the following terms: (*a*) kindling temperature; (*b*) spontaneous combustion; (*c*) heat of oxidation; (*d*) products of oxidation.

20. What is the weight of 100 liters of oxygen? (See Appendix F for weight of 1 liter of various gases.)

21. (*a*) What name do we give to the substance formed when an electrical discharge is passed through oxygen? (*b*) Mention three ways in which this substance differs from oxygen. (*c*) How do we account for this difference in properties?

THOUGHT QUESTIONS

✓ 1. (*a*) Can you tell from the looks of a compound whether it contains oxygen? (*b*) Give two examples which prove your answer correct.

2. Why do we call oxygen an element and potassium chlorate a compound?

✓ 3. What chemical action is prevented by painting houses and metal structures such as iron bridges?

4. (*a*) State the chemical changes involved in preparing oxygen from mercuric oxide, from water, and from potassium chlorate. (*b*) What product other than oxygen is obtained in each case?

5. Name two kinds of energy used in liberating oxygen from its compounds.

6. Suppose that oxygen were very soluble in water. How could you collect it?

7. Neither oxygen nor sulfur has any odor. How do you account for the very marked odor that always accompanies the burning of sulfur in oxygen?

8. (*a*) What elements have you burned in oxygen? (*b*) Suggest a name for each of the products formed.

9. State the phlogiston theory of combustion and show a fundamental weakness in it (see Introductory Chapter).

10. Many of us use gas in our homes with perfect safety for heating, cooking, and lighting. Yet we sometimes read of houses being blown to pieces from gas explosions. How do you account for such explosions?

11. Give, with the reason, each step you would take in starting a coal fire.

12. Is emission of light a sure proof of combustion?

✓ 13. Why do you blow a candle flame to extinguish the flame but blow a glowing coal to start the flame?

FOR HONOR STUDENTS

1. Suggest different methods for putting out a fire, and explain how each would act.

2. Three students prepared oxygen. One decomposed 100 g. of water, another 100 g. of mercuric oxide, and the third, 100 g. of potassium chlorate. What weight of oxygen did each obtain?

3. A student prepared oxygen by heating in a flask 40 g. of potassium chlorate mixed with 5 g. of manganese dioxide. (*a*) What weight of oxygen was obtained? (*b*) What volume would this weight of oxygen occupy? (*c*) What compounds remained in the flask? (*d*) Calculate the weight of each.

4. Write a brief biographical sketch of either Priestley or Lavoisier. (Consult an encyclopedia.)

CHAPTER IV

HYDROGEN

The Lightest of All Elements

57. *Introduction.* During the World War we often read of the huge airships that sailed out of Germany trying to destroy the fighting powers of the Allied nations. Since the war these airships, or Zeppelins, as they are often called (from the engineer who constructed the first one), have crossed and recrossed the ocean and even circled the world without loss of life; and many believe that it will not be long before the traveler who wishes to visit Europe may take his choice between an ocean liner and an airship (see frontispiece).

For these ships to float in the air it is necessary that they have as an essential part a large container or envelope filled with some very light gas. One of the gases selected for this purpose is hydrogen, since it is the lightest of all gases, being more than fourteen times lighter than air. This is only one of the many uses of hydrogen. We shall find, as we proceed, that much larger amounts of the gas are used in transforming oils into solid fats and in manufacturing important compounds, among them some of our most valuable fertilizers. It is also a constituent of most of our fuel gases, such as coal gas and water gas. Hydrogen, therefore, is one of the important elements for our study.

58. Where is hydrogen found? Hydrogen is not nearly so abundant as oxygen (§ 23); moreover, it differs from oxygen in that only very small amounts of the element occur on the earth in the free state. True, it occurs in the atmosphere, but in amounts so small that only the trained chemist can detect it. Its compounds, however, are everywhere abundant. Water, our foods, our bodies, all contain hydrogen. Combined with carbon it forms many compounds which, mixed together, constitute petroleum and natural gas. While only traces of free hydrogen occur on the earth, it is a remarkable fact that the free element occurs in enormous quantities in the gases surrounding the sun and certain other stars. How to account for this fact is a question of great interest.

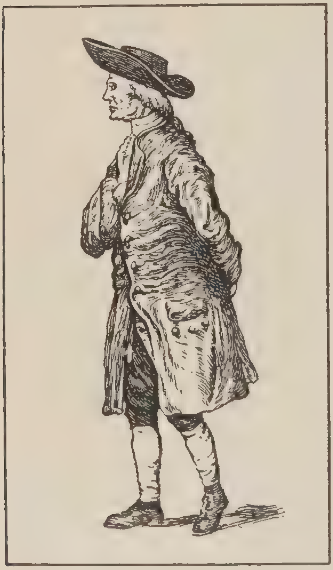


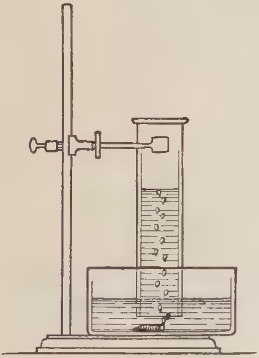
FIG. 27. Henry Cavendish (1731–1810)

A famous English scientist, contemporary with Joseph Priestley. He described hydrogen as a new gas, and showed that it produced water when burned

59. The discovery of hydrogen. At the same time that Priestley was experimenting with gases, another Englishman, Henry Cavendish (Fig. 27), was busy trying to find out the nature of these forms of matter. Many of the early chemists had observed the fact that when the liquids we now term *acids* were poured over certain metals such as iron the metal gradually disappeared, and bubbles of gas were evolved. Cavendish collected some of it and studied its properties. In 1766 he obtained it in pure state, and proved it to be different from all other known gases. Cavendish called it *inflammable air* because it burns so readily. Later, Lavoisier named it *hydrogen*, a word signifying "producer of water"; for when it burns, water is formed.

60. Preparation. Hydrogen can be prepared in a number of ways, the most important of which are the following:

1. ***Preparation from water.*** Since water contains hydrogen and is so abundant, it is but natural that we should try to obtain the element from this source. It is possible to liberate the hydrogen in water in two general ways: (*a*) we may use the method of electrolysis already described (Fig. 17) and in this way obtain both hydrogen and oxygen, or (*b*) we may act on water with certain elements which will combine with the oxygen of the water and liberate the hydrogen. For this purpose some of the metals serve our purpose best. In the case of a few of the metals this change occurs at ordinary temperatures. Thus, if a bit of the metal *sodium* is dropped on water, an action is seen to take place at once, sufficient heat being set free to melt the sodium, which runs about on the surface of the water. The change which takes place consists in the substitution of sodium for half of the hydrogen of the water, and may be represented as follows:



Since the sodium is lighter than water, it is kept under the water by pushing a pellet of the metal into one end of a short piece of lead or tin pipe, the other end of which has been hammered flat. The pipe containing the sodium is then dropped into water, and a cylinder or bottle entirely filled with water is suspended over it. The hydrogen is at once evolved, and collects in the cylinder as shown in the figure

FIG. 28. Preparation of hydrogen by the action of sodium on water

$$\underset{\text{sodium}}{\mathrm{Na}} + \underset{\text{water, }H_2O}{\mathrm{HOH}} \longrightarrow \underset{\text{hydrogen}}{\mathrm{H}} + \underset{\text{sodium hydroxide}}{\mathrm{NaOH}}$$

The sodium hydroxide formed remains dissolved in the excess of undecomposed water, and may be obtained as a white solid by evaporating the solution to dryness. The hydrogen is evolved as a gas and may be collected as shown in Fig. 28.

Other metals, such as *magnesium* and *iron,* decompose water rapidly, but only at higher temperatures. When steam is passed over sufficiently hot iron, for example, the iron combines with the oxygen of the steam, forming iron oxide and setting free all the hydrogen as a gas (Fig. 29).

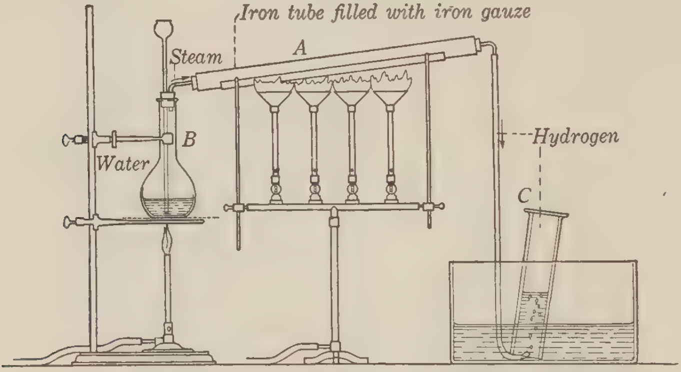


FIG. 29. Preparation of hydrogen by passing steam over hot iron

The steam, generated by heating the water in flask *B*, passes through the tube *A*, which is filled with hot iron gauze. The oxygen in the steam combines with the hot iron, thus liberating the hydrogen. The hydrogen passes on and is collected over water in the cylinder *C*

2. ***Preparation from acids (usual laboratory method).*** The *acids* constitute a very important class of compounds, and we shall be much occupied with them later in our study. For the present it is only necessary to know that they all contain hydrogen and that certain metals when brought in contact with them dissolve, and in the change which takes place the hydrogen of the acid is liberated. This gives us a convenient method for preparing hydrogen in the laboratory (Fig. 30).

It has been found most convenient and economical in preparing hydrogen by this method to use either *zinc* or *iron* as the metal and either *hydrochloric acid* or *sulfuric acid* as the acid. Hydrochloric acid is an aqueous solution of a gaseous compound known as hydrogen chloride (which consists of 2.77 per cent hydrogen and 97.23 per cent chlorine), while sulfuric acid is an aqueous solution of an oily liquid known as hydrogen sulfate (which consists of 2.05 per cent hydrogen, 32.70 per cent sulfur, and 65.25 per cent oxygen). These are the two common acids.

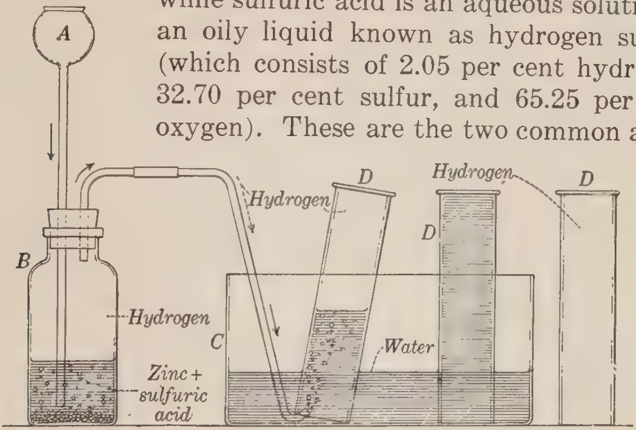


FIG. 30. The preparation of hydrogen from acids

The metal (zinc or iron) is placed in the flask *B* and the acid (dilute sulfuric or hydrochloric) is added slowly through the funnel tube *A*. The metal displaces the hydrogen in the acid. The hydrogen thus liberated escapes through the exit tube and is collected over water in the jars *D, D, D*

The changes taking place in the preparation of hydrogen from zinc and sulfuric acid may be represented as follows:

$$\mathrm{Zn} + \underset{\text{sulfuric acid}}{\mathrm{H_2SO_4}} \longrightarrow \underset{\text{zinc sulfate}}{\mathrm{ZnSO_4}} + 2\,\mathrm{H}$$

In other words, the zinc takes the place of the hydrogen in sulfuric acid. The resulting compound contains zinc, sulfur, and oxygen, and is known as *zinc sulfate*. This remains dissolved in the water in the acid. It may be obtained in the form of a white solid by evaporating the liquid left after the metal has passed into solution.

61. Physical properties. Like oxygen, hydrogen is a colorless, tasteless, odorless gas, very slightly soluble in water. Its most characteristic property is its extreme lightness, 1 liter of it weighing only 0.08987 g., or, in round numbers, 0.09 g. Pure hydrogen is not poisonous; but we could not live in an atmosphere of the gas, because we must have oxygen.

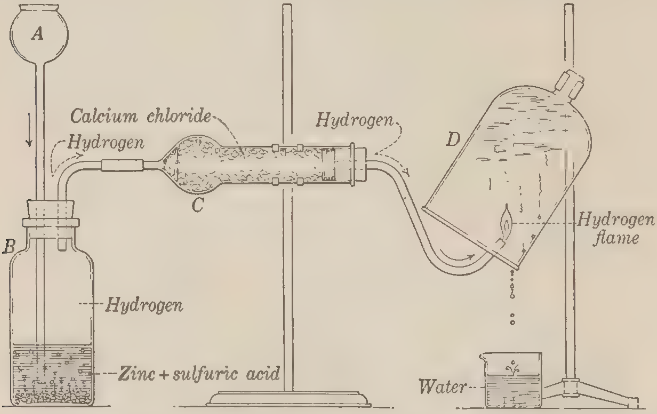


FIG. 31. Burning hydrogen in air and collecting the product of its combustion (water)

The hydrogen is generated in the bottle B, and is dried by conducting it through the tube C, filled with calcium chloride, which has a great attraction for moisture, and escapes through the tube, which is drawn out to a jet as shown in the figure. *When all the air has been expelled from the apparatus* the hydrogen is ignited. It then burns quietly, since only the small amount of it which escapes from the jet at any one moment can come into contact with the oxygen of the air. By holding a cold dry bell jar D over the flame as shown in the figure, the steam formed by the combustion of the hydrogen is condensed. The water collects in drops and falls into the beaker

62. Chemical conduct. At ordinary temperatures hydrogen is not an active element. At higher temperatures, however, it combines with many of the elements forming compounds, the most important of which is water. If we mix hydrogen and oxygen at room temperatures, no action takes place. If the mixture is heated to about 800°, or if a flame is brought in contact with it, the two gases combine with explosive violence. By choosing the right conditions, however, we can cause the two gases to combine with perfect safety. This can best be done by burning a stream of pure hydrogen in pure oxygen or in air (Fig. 31). The flame produced is, however, unlike most flames with which you are familiar. It can hardly be seen, but is very hot. The combustion is due to the direct union of the hydrogen and oxygen, and the product is ordinary water.

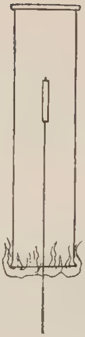


FIG. 32. Flame of a candle extinguished by hydrogen

63. Hydrogen not a supporter of combustion. While hydrogen is readily combustible, it is not a supporter of combustion; in other words, substances will not burn in it. This may be shown by bringing a lighted candle supported by a stiff wire into an inverted bottle or cylinder of the *pure* gas, as shown in Fig. 32. The hydrogen is ignited by the flame of the candle and burns at the mouth of the cylinder, where it comes in contact with the oxygen in the air. When the

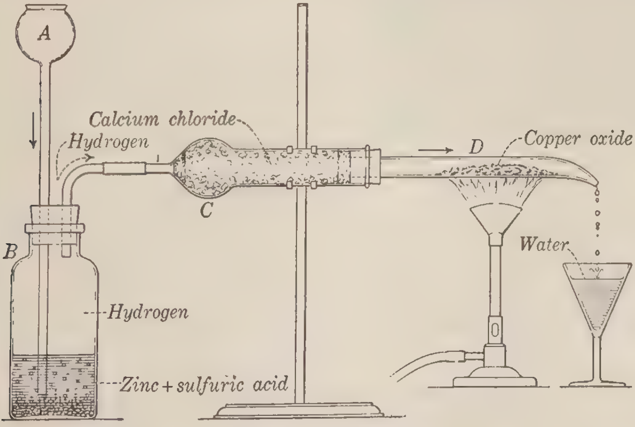


FIG. 33. The reduction of hot copper oxide by a stream of hydrogen

candle is thrust up into the gas its flame is extinguished. If slowly withdrawn, the candle is relighted as it passes through the place where hydrogen is burning.

64. Reduction and its relation to oxidation. On account of its tendency to combine with oxygen, hydrogen has the power of taking oxygen away from many of its compounds. Thus, if a stream of hydrogen generated in *B* (Fig. 33) and dried by passing through the tube *C* (filled with calcium chloride) is conducted through the tube *D*, which contains some copper oxide heated to a moderate temperature, the hydrogen takes away the oxygen from the copper oxide. The change may be represented as follows:

$$\underset{\text{copper oxide}}{CuO} + 2\,H \longrightarrow \underset{\text{copper}}{Cu} + H_2O$$

The water formed collects near the end of the tube *D* and drops into the glass. In this experiment the copper oxide is said to be *reduced*, and the process is known as *reduction*. While the chemist sometimes uses the term in a broader sense, for the present we may define reduction as *the process of withdrawing oxygen from a compound.*

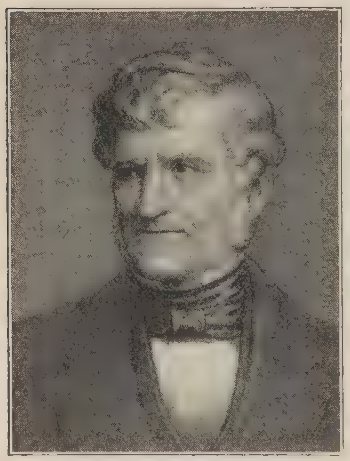


FIG. 34. Robert Hare (1781–1858)

An early American chemist, who invented the oxyhydrogen blowpipe

If we study the action of hydrogen on copper oxide as given above, we see that at the same time the oxide is reduced the hydrogen is oxidized. *The processes of reduction and oxidation are therefore the opposite of each other;* the one consists in withdrawing oxygen from a compound and the other in adding oxygen to another element or compound.

Hydrogen or any other element or compound that readily combines with oxygen and is capable of withdrawing it from its compounds is known as a *reducing agent*; while oxygen or any compound (such as copper oxide or potassium chlorate) that readily gives up oxygen is known as an *oxidizing agent.*

65. The oxyhydrogen blowpipe; the blast lamp. We have seen that when hydrogen burns in oxygen the flame is very hot; it is so hot, indeed, that by means of it we can melt all the ordinary metals, and even platinum, which has a melting point (1755°)[1] much higher than that of iron. It is natural that chemists should have tried to utilize this heat for many purposes. The American chemist Robert Hare (Fig. 34) was the first to devise a satisfactory apparatus for burning the hydrogen in oxygen so that the heat could be utilized. This apparatus is called the *oxyhydrogen blowpipe.* While it is no longer in use to any extent, similarly constructed blowpipes are utilized in which gaseous compounds of hydrogen are used in place of pure hydrogen (§ 458). The ordinary blast lamp of the laboratory is practically a large oxyhydrogen blowpipe. It consists of two tubes, one inside the other (Fig. 35). Some form of fuel gas, such as coal gas or natural gas (both of which are composed chiefly of compounds of hydrogen and carbon) is forced through the outer tube and ignited at the end of the tube. Sufficient air is then forced through the inner tube to render the flame nearly colorless.

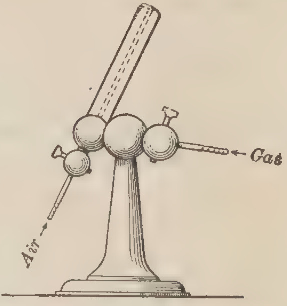


FIG. 35. The ordinary laboratory blast lamp

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[1] All temperature figures in the book refer to the centigrade scale. A comparison of this scale with the Fahrenheit scale will be found in Appendix B.

CHAPTER SUMMARY IN QUESTION FORM

1. Give the form (free or combined) and relative abundance of hydrogen in each of the following: (*a*) earth's crust; (*b*) water; (*c*) earth's atmosphere; (*d*) sun's atmosphere.

2. (*a*) Who first obtained hydrogen in a pure state? (*b*) Who gave it its present name?

3. Give two general ways of preparing hydrogen from water.

4. Name the products of the reaction of sodium on water.

5. Name the products of the reaction of iron on steam.

6. (*a*) What element is present in all acids? (*b*) How can you set it free?

7. Explain in detail the usual laboratory method for preparing hydrogen, giving the names of the substances used and the products formed in the reaction.

8. Mention one very important precaution that should be taken in preparing hydrogen.

9. Compare hydrogen and oxygen as to (*a*) weight; (*b*) color; (*c*) odor; (*d*) taste; (*e*) solubility in water; (*f*) effect on body when inhaled.

10. In the ordinary meaning of the term, should you say that hydrogen burns or that it supports combustion?

11. What two properties of hydrogen are shown by thrusting a lighted taper up into an inverted cylinder of the gas?

12. Copper oxide plus hydrogen gives copper plus water. What is the action (*a*) of the hydrogen on the copper oxide? (*b*) of the copper oxide on the hydrogen?

13. Give two practical uses of hydrogen.

14. Draw a diagram of the laboratory blast lamp and explain the way it works.

THOUGHT QUESTIONS

1. Zinc is an element and solid, yet bubbles of gas rise from it when it is placed in sulfuric acid. Explain.

2. Should you expect free hydrogen and free oxygen to occur in nature? Explain.

3. What factors determine the choice of preparing a substance (*a*) in the laboratory? (*b*) commercially, that is, on a large scale?

4. In Fig. 33 why do we dry the hydrogen before passing it over the copper oxide?

5. Which explodes the more violently, a mixture of hydrogen and oxygen or a mixture of hydrogen and air? Explain.

6. Explain what takes place when a lighted candle is thrust into a cylinder (*a*) of hydrogen; (*b*) of air; (*c*) of oxygen; (*d*) of a mixture of hydrogen and air; (*e*) of a mixture of hydrogen and oxygen; (*f*) of a mixture of oxygen and air.

7. What is the great objection to the use of hydrogen as a material for inflating balloons for war purposes?

8. Hydrogen passed over hot copper oxide forms water and copper. What does this prove in regard to the composition of water?

9. Why does the oxyhydrogen blowpipe give a hotter flame than the blast lamp?

10. An ordinary five-cent piece weighs about 5 g. (*a*) What volume of hydrogen would weigh a like amount? (*b*) What volume of oxygen?

11. Suppose you have a quantity of sulfuric acid containing 100 g. of hydrogen sulfate. (*a*) What weight of hydrogen is present in it? (*b*) If you liberate this hydrogen, what volume will it occupy?

FOR HONOR STUDENTS

1. Devise a simple experiment to show that hydrogen is much lighter than either oxygen or air.

2. Suppose you wished to inflate a small balloon having a capacity of 1000 liters of hydrogen. (*a*) What weight of hydrogen would be required? (*b*) What weight of hydrogen sulfate would be required to prepare sufficient hydrogen to inflate the balloon?

3. Water, as has been stated, contains about eight times as much oxygen as hydrogen by weight. Yet when we decompose water by the electric current the oxygen obtained has only half the volume of the hydrogen (Fig. 17). Explain.

CHAPTER V

STATES OF MATTER

Solid, Liquid, Gaseous

66. ***Introduction.*** Suppose we recall a great many material objects with which we are acquainted, such as water, the soil, rocks, trees, air, our bodies; they are all either solids or liquids or gases. Our daily experiences teach us much more about liquids and solids than about gases; for we can see liquids and solids and easily handle them, but most gases are invisible and all the common ones that make up our atmosphere are odorless, so that while we are constantly immersed in a sea of gases we are rarely aware of their presence unless a strong wind is blowing. In the early days of history it was supposed that gases had no weight, and there was a great deal of mystery about them. Today we know that they are simply another form of matter.

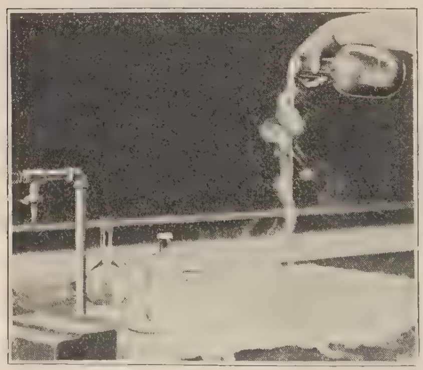


FIG. 36. Pouring liquid air from a thermos bottle onto a laboratory desk

While these three states of matter have very different properties, there are many substances that may be obtained in any one of the three, and the change from any one state into any other is purely a physical change. We think of water as a liquid, but we can easily change it into a solid (ice) or into a gas (steam). *Liquid* air (Fig. 36) can be purchased on the market like sugar or coal, and the gas carbon dioxide, which we exhale from our lungs, is sold in solid form called *dry ice* (Fig. 37) and used to keep ice cream from melting.

67. Representation of definite amounts of matter. Solids are easily weighed, so it is convenient to refer to any definite amount of a solid by telling how much it weighs. We buy sugar by the pound, and coal by the ton. It is easy to weigh liquids also, but it is simpler to pour them into a graduated vessel or some standard measure and obtain their volumes; so we buy gasoline by the gallon and milk by the quart. Gases are so light that it is difficult to weigh them; as a result, we generally refer to any definite amount of gas by giving its volume. Our monthly gas bill demands payment for a certain number of cubic feet of gas. In determining the volume of a gas, we have to keep in mind that the volume of any gas easily changes with the pressure to which it is subjected, and also with its temperature. It is important, therefore, that we should know something about these changes.

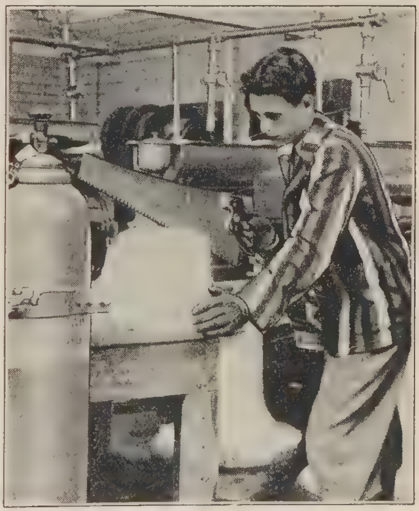


FIG. 37. Sawing a block of solid carbon dioxide into slabs for packing ice cream

68. The volume of a gas changes with the pressure; Boyle's law. Everyone who has pumped up an automobile tire knows that a large amount of gas can be compressed into a relatively small space. In some respects a gas acts like a coiled spring. By compressing the spring it can be made to occupy a small space; but if the pressure is gradually diminished the spring keeps expanding, filling a larger and larger space.

FIG. 38. Robert Boyle (1627–1691)

The first to define an element and to show that a compound is made up of two or more kinds of elements. Chiefly remembered for experiments with gases

The great scientist Robert Boyle (Fig. 38) was the first to show the exact relation between the volume occupied by a gas and the pressure to which it is subjected, and his statement of this relation, first made in 1660, is known as Boyle's law. This may be stated as follows: *The volume occupied by a given weight of gas varies inversely with the pressure, provided the temperature of the gas remains constant.* For example, let us suppose that a given weight of gas occupies a volume of 1000 cc. when subjected to a certain pressure. If now the pressure is doubled, the gas will occupy a volume of only 500 cc.; if half the pressure is taken off, the volume of the gas will increase to 2000 cc.

69. The volume of a gas changes with the temperature; Charles's law. The volume of a gas depends not alone on pressure; it varies also with temperature. "Heated air expands" is a well-known saying, and this statement holds good for all gases. Temperature and pressure, then, have opposite effects upon the volume occupied by a gas. Increasing the temperature increases the volume; increasing the pressure diminishes the volume. The relation between the volume and temperature of a gas is expressed in Charles's law, which may be stated as follows: *The volume occupied by any given weight of gas increases by $\frac{1}{273}$ of the volume it occupies at 0° for each degree its temperature is raised, provided the pressure remains constant; likewise its volume is decreased $\frac{1}{273}$ of the volume it occupies at 0° for each degree its temperature is lowered.* For example, if a gas had a volume of 1000 cc. at 0°, its volume at $+1°$ would be $1000 + \frac{1000}{273}$, or 1003.6 cc.; at $+10°$ it would have a volume of $1000 + 10 \times \frac{1000}{273}$, or 1036 cc., and at $-10°$ it would be $1000 - 10 \times \frac{1000}{273}$, or 964 cc.

If we know the volume occupied by any given weight of gas at some definite pressure and temperature, the laws of Boyle and Charles make it possible to calculate the volume which the same gas will occupy at any other pressure and temperature. It is sometimes convenient to make such calculations, and the method used is given in Appendix C for the benefit of those who may care to go further into this subject.

70. Standard conditions. Facing the back cover of this text is a table giving the weight of 1 liter of each of the common gases. These values are of interest, for if we know the volume of any particular gas the table enables us to calculate the *weight* of this volume of the gas. Likewise, if we know the weight of the gas we can calculate the volume which it will occupy.

But since the volume of a gas varies with the pressure as well as with the temperature, the statement that 1 liter of oxygen weighs 1.4290 g. (see table) really means nothing unless we know the temperature and pressure under which the oxygen was measured. In order to have uniformity, scientists have agreed upon certain *standard conditions* of temperature and pressure, namely, a temperature of 0° and a pressure equal to the average pressure exerted by the atmosphere at the sea level, that is, 1033 g. per square centimeter. When we say that 1 liter of oxygen weighs 1.4290 g. we mean that the amount of oxygen which has a volume of 1 liter when measured at 0° under a pressure of 1033 g. per square centimeter weighs 1.4290 g.

71. Changes of heat when a gas is compressed or allowed to expand. Everyone who has inflated an auto tire with a hand pump knows that the pump gets hot by the heat liberated in compressing the air. Moreover, if the air in an inflated tire is allowed to escape, the escaping air is distinctly cooler than the surrounding air. Thus we see that *heat is liberated when a gas is compressed, and is absorbed when a gas expands.* We shall see that these heat changes are of great importance in understanding how gases are liquefied.

72. Theories and their uses. We are all naturally more or less curious. We are not satisfied with knowing *that a certain thing is so*; we want to know *why it is so*, and if we cannot find out we begin to make guesses as to why it is so. When we are doing this we are really making a theory, a crude one probably, but one that we may test and see if our guesses satisfactorily account for the facts. If they do not, we modify the guesses or make new ones that will. In this way we gradually build up a theory. If it is a satisfactory one, it will not only enable us to explain the known facts; it will also help us to discover new ones. A theory, then, *is simply a guess or a collection of guesses by which we can explain in a satisfactory way certain facts whose real cause is unknown.*

Now we have learned certain facts about gases: (1) they exert a pressure on the walls of any vessel in which they are confined; (2) they tend to expand indefinitely, and will do so unless confined in a closed vessel; (3) they contract when subjected to pressure; and (4) they expand when heated. How can we account for these facts? About one hundred years ago, the English scientist John Dalton (Fig. 57) advanced certain ideas to account for the properties of gases, and these ideas were later developed into a theory which is known as the *kinetic theory of gases.*

73. The main points of the kinetic theory. The main points of the kinetic theory may be stated very briefly as follows: (1) all gases are made up of very minute particles which we call *molecules*; (2) all the molecules of the same gaseous element or compound are exactly alike, but the molecules of different elements or compounds are unlike, at least in weight and composition; (3) the molecules are in very rapid motion, like the bees in a swarm, and are constantly hitting each other and the sides of any containing vessel and rebounding; (4) when a gas is heated, the motion of the molecules is increased.

Let us now see if this theory accounts for the facts we have learned about gases. Since the molecules are definite particles and are in very rapid motion, they would hit the sides of any containing vessel, thus exerting a pressure. If not confined they would tend to fly away; in other words, the gas would tend to expand indefinitely. The molecules do not fill all the space in a room; hence, when we compress a gas we simply crowd the molecules more closely together. They will hit the sides of the vessel oftener and so exert more pressure. Heat increases the motion of the molecules so that they will hit the walls of the containing vessel with greater force, and the gas will thus tend to expand.

These guesses which constituted the kinetic theory are now known to be true. We know that the molecules exist, and we can even compute the number of them in a given volume of gas with greater accuracy than we can count the number of people who live in a large city. Though we still speak of the kinetic theory, it is really no longer a theory but a statement of fact.

74. The nature of solids and liquids. We know from our experiments that not only gases, but solids and liquids as well, are made up of molecules. Moreover, all the molecules of the same element or the same compound are always exactly alike. In a solid the molecules are crowded together and have such a strong attraction for each other that the shape of the solid is not easily changed. In liquids the molecular motion is greater, and a liquid adjusts itself to the shape of any containing vessel. In gases the motion of the molecules is so great that the attractive forces are entirely overcome.

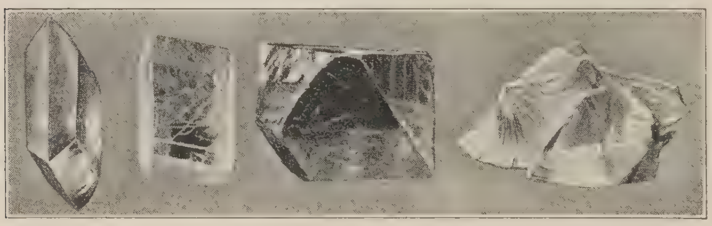


FIG. 39. Some specimens of crystals as they are found in nature

75. Amorphous and crystalline matter. Sometimes the particles of which a piece of solid matter is composed have no definite form, and even under the microscope show no sharp edges or flat surfaces. Such solids are said to be *amorphous*.

More often a careful examination of a solid will show that it is made up of a great many particles, each of which has sharp edges and flat surfaces. Such solids are said to be *crystalline*, and each individual piece is called a *crystal*. Crystals have a great variety of forms (Fig. 39), but for any given substance the crystalline form is perfectly definite. Crystals range in size from microscopic to very large. Crystals of the mineral beryl have recently been found in Maine that are from 12 to 14 ft. long and from 2 to 3 ft. in diameter.

76. Freezing point and melting point. Let us suppose that we place a beaker of pure water in a freezing mixture

(Fig. 40) and stir the water with a thermometer so that we can watch its temperature and at the same time keep the temperature uniform throughout the liquid; what will happen? Everyone knows that the temperature will fall to 0°; but the interesting thing to note is that *the temperature of the water will then remain constant at 0° until all the water is frozen.* The temperature of the resulting ice will then fall to that of the freezing mixture. The constant temperature during the changing of the liquid to the solid form is called the *freezing point* of the liquid.

If now we remove the beaker from the freezing mixture the reverse changes take place. The ice soon reaches a temperature of 0°, when it begins to melt; *the temperature then remains at 0° until all the ice has melted,* after which it will slowly rise to the temperature of the room. It is important to note that *the freezing point of water and the melting point of ice are the same.*

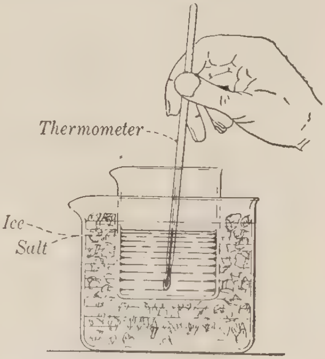


FIG. 40. Measuring the freezing point of water

What is true of ice is also true of all crystalline solids: they all have a definite melting point (or point of fusion). The resulting liquids have a definite freezing point (or point of solidification), and *the freezing point and the melting point are always identical for the same substance* but differ widely for different substances. Thus, ice melts at 0°, lead melts at 327.5°, and gold at 1063°.

Amorphous (noncrystalline) substances have no sharp melting point, but gradually pass from the solid to the liquid state as the temperature rises. Under unusual conditions a liquid fails to solidify at the freezing point and remains liquid below that point. It is then said to be *undercooled.*

77. The unit of heat. To understand the heat changes that take place when a solid melts or a liquid freezes, it is necessary for us to know the unit used in measuring *quantity of heat.* We use a thermometer or some similar device for measuring *intensity* of heat, or temperature. Evidently temperature alone is no measure of *quantity* of heat, for the temperature of a large volume of hot water and that of a cupful dipped from it are the same, yet the quantity of heat in the two is vastly different. The common unit which has been adopted for measuring quantity of heat is called the *calorie,* and is defined as follows: *The calorie is the quantity of heat required to raise the temperature of 1 g. of water 1° C.* It is represented by the abbreviation *cal.*

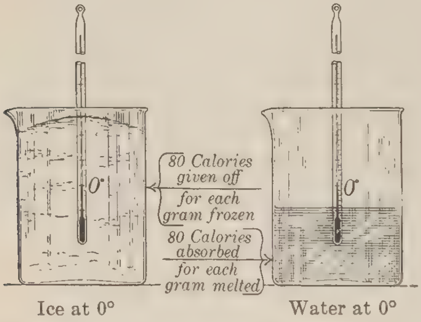

0°
80 Calories given off for each gram frozen
80 Calories absorbed for each gram melted
0°
Ice at 0°
Water at 0°

FIG. 41. The heat of solidification and the heat of fusion

78. Heat changes during freezing and melting. We have seen that the freezing point of water and the melting point of ice are identical. In the change of water at 0° into ice at 0° heat is given out. *The heat evolved during the change of 1 g. of a liquid at its freezing point to a solid at the same temperature is called the heat of solidification of that liquid.* For water this is 80 cal. In other words, the heat evolved when 1 g. of water at 0° changes into ice at 0° is 80 cal. (Fig. 41).

When the resulting ice at 0° is melted this heat change is reversed and 80 cal. of heat are absorbed (Fig. 41). *The heat absorbed when 1 g. of a solid at its melting point is changed into a liquid at the same temperature is known as the heat of fusion of the solid.* For the same substance *the heat of solidification and the heat of fusion are identical.*

79. Vapors; vaporization. Water as well as most other liquids, when exposed to the air, gradually disappears. We say that the water *evaporates*. What happens is, of course, that the water changes from the liquid state into the gaseous. If a substance is liquid or solid at ordinary temperatures, as water is, its gaseous form is commonly called a *vapor*, so that we speak of the vapor of water and not of the gas of water.

The change of water into vapor is due to the fact that the molecules of the liquid are in violent motion, and, though they have an attraction for each other, some of them at the surface of the liquid are constantly breaking away and escaping into the air. This process goes on at all temperatures, but since heat increases the motion of the molecules we should expect the rate of evaporation to increase with the temperature, and it does.

The molecules of solids are also in constant but slower motion, and their attraction for each other is so strong that we might not expect them to escape into the air like those of liquids; yet we find that many solids do evaporate, although the rate is so slow that we do not notice it ordinarily. Many of us have observed that the well-known moth balls, when exposed to the air, gradually grow smaller and finally disappear; and the odor of many solids is direct evidence that they evaporate.

80. Boiling point. Suppose we heat a liquid in an open vessel, say water in a beaker. The water evaporates, and the resulting vapor escapes into the air. Its escape, however, is hindered by the air which presses upon the surface of the liquid. As the temperature rises, the rate of evaporation increases, and finally reaches a point where the pressure of the vapor just exceeds the downward pressure exerted by the air. When this point is reached there is nothing to prevent the vapor from making its escape as fast as it forms, pushing the air before it. When this is the case any additional heat applied to the liquid *will not raise its temperature, but will merely increase its rate of evaporation.*

This temperature is called the boiling point of the liquid, and the boiling point may be defined as *the temperature at which the vapor pressure of the liquid just exceeds the opposing pressure of the atmosphere.* It will be noticed that the boiling point of a liquid is not fixed, but depends upon the atmospheric pressure. When we say that water boils at 100°, we mean that it boils at this temperature when the atmospheric pressure is the average of the pressure at the sea level, namely, 1033 g. per square centimeter. At Mexico City (elevation 7000 ft.) water boils at 93°, while on the top of Mt. Everest (elevation 29,000 ft.) it would boil at 72°.

81. Heat of vaporization. Just as the change of a solid into a liquid or vice versa is accompanied by certain heat changes, so, when a liquid vaporizes or a vapor condenses, there are similar heat changes. The heat absorbed when 1 g. of a liquid at its boiling point is changed into a vapor at the same temperature is known as the *heat of vaporization* of that liquid. For water this amounts to 537 cal. When the resulting steam condenses to a liquid this heat change is reversed and 537 cal. are evolved (*heat of condensation*).

82. Changing gases into liquids. We have seen (§ 66) that air and carbon dioxide, two of our common gases, may be obtained in a liquid or even in a solid state. How is this change brought about? The main difference between a liquid and a gas is that in the liquid the molecules are moving much more slowly and are crowded more closely together, so that the attraction which they have for each other is increased. This crowding can be brought about by compressing the gas. Cooling the gas would also have the same effect, for the velocity of the molecules is diminished by cooling and so they would not have the same tendency to fly away from each other. Many gases may be liquefied by pressure alone or by cooling alone. Some, however, are very difficult to liquefy, and the liquefaction of these requires the combined effect of both cooling and pressure. Every known gas has now been liquefied; helium, the most difficult of all to liquefy, was obtained in a liquid state in 1908. The resulting liquids have definite boiling points and freezing points just as water has. Thus, liquid oxygen boils at − 183° and freezes at − 218.4°; liquid hydrogen has a still lower boiling point (− 252.7°); liquid helium has the lowest of all, namely, − 268.9°.

CHAPTER SUMMARY IN QUESTION FORM

1. Name the three states of matter, giving an example of each.

2. Give an example of a substance that may exist in each of the three different states.

3. What is the usual unit used in measuring each of the states of matter?

4. Give two ways of changing the volume of a gas, and illustrate each with an example.

5. State Boyle's law.

6. State Charles's law.

7. What are the standard conditions used in measuring the volumes of gases?

8. What is understood when we state that 1 liter of oxygen weighs 1.429 g.?

9. What heat changes take place (*a*) when air is forced into an automobile tire? (*b*) when the valve on a tire is removed, thus allowing the air to escape?

10. (*a*) What is a theory? (*b*) How do theories differ from facts?

11. Give the four chief points of the kinetic theory.

12. Show how the kinetic theory accounts for the properties of gases.

13. Are the molecules of the same element or compound identical or different?

14. Contrast the properties of a gas with those of a liquid and those of a solid.

15. (*a*) What name do we apply to substances like sawdust, whose particles have no definite form? (*b*) What name to substances like a diamond, whose particles have flat surfaces and sharp edges?

16. Explain all that takes place when water is cooled from 5° above zero to 5° below zero, and when it is warmed from the latter temperature to the former.

17. Give the name of the unit of heat and define it.

18. (*a*) What is meant by the term *melting point*? (*b*) What kind of substances has a definite melting point?

19. (*a*) What is meant by the term *freezing point*? (*b*) How does the melting point of a substance compare with its freezing point?

20. Suppose you draw some water from the tap and heat it until it is all boiled away. Explain all the heat changes that take place.

21. Explain what is meant by the terms (*a*) heat of fusion; (*b*) heat of solidification; (*c*) heat of vaporization. Give the value of each of these as applied to water.

22. Distinguish between gases and vapors.

23. State two means by which the molecules of a gas can be crowded together, thus liquefying it.

THOUGHT QUESTIONS

1. You cannot see, taste, hear, feel, or smell the air in a quiet room. How, then, can you prove that air is really a form of matter?

2. Point out a possible source of error in the following reasoning: "I filled a 500-cc. flask with oxygen in the laboratory. This must weigh 0.7145 g., since the table in Appendix F gives the weight of 1 liter of oxygen as 1.429 g."

3. (*a*) Does a theory ever become a fact? (*b*) Does a fact ever become a theory?

4. When air is compressed, heat is given off; when it expands, heat is absorbed. Explain where the heat comes from in the first case, and what becomes of it in the second.

5. (*a*) Is heat a form of matter or of energy? (*b*) When heat is applied to boiling water, the temperature is not raised; what becomes of the heat that is being applied?

6. (*a*) How could you prevent the expansion of a gas when heated? (*b*) Might any danger result from this procedure?

7. Suggest a way of raising the boiling point of water above 100°.

8. Suggest two reasons why you would have trouble in cooking vegetables on the top of Pikes Peak.

9. Some people place tubs of water in their cellars on very cold nights, believing that this will prevent the vegetables from freezing. Do you think this is sound reasoning?

10. 50 lb. of ice at 0° is placed in a refrigerator. How many calories of heat are absorbed in its melting? (See Appendix F for number of grams in 1 lb.)

FOR HONOR STUDENTS

1. State some important fact the explanation of which is unknown to you; then form a theory that would account for the fact.

2. Give the names of all the great chemists mentioned so far in our study, and state one important discovery of each.

3. 1 liter of water at 10° was heated until it all boiled away. How many calories of heat were absorbed in the process?

4. 100 lb. of ice were placed in a refrigerator. It melted, and the resulting water flowing from the refrigerator had a temperature of 10°. How many calories of heat were absorbed from the interior of the refrigerator?

5. A gas under standard conditions measured 100 liters. Suppose its temperature was raised to 50° and at the same time the pressure upon it was doubled; what volume would it then occupy?

CHAPTER VI

WATER

The Most Important Liquid in the World

83. ***Introduction.*** Aside from petroleum, water is the only liquid found extensively in nature. It covers about five sevenths of the surface of the earth, in some places to a depth of five or six miles. It is a constituent of many rocks, of the atmosphere (in the form of vapor), and of every plant and animal that grows. If you weigh 150 lb., over 100 lb. (70 per cent of your weight) is water. If you buy 100 lb. of such food as meat, vegetables, and fruit, you buy at least 75 lb. of water; and if you confine your purchases to celery, tomatoes, lettuce, and spinach, the weight of water purchased exceeds 90 lb. Even dry-looking things, such as wood, coal, and many minerals, yield water when heated. Some astronomers can find nothing but water over the entire surface of the planet Venus. Indeed, the whole chemistry of our world is a water chemistry, and to all living things water is of supreme importance.

84. The discovery of the composition of water. Until about a hundred and fifty years ago water was supposed to be an element, and there was a great stir among scientific men when Cavendish (Fig. 27), coöperating with Lavoisier (Fig. 20), proved it to be a compound of hydrogen and oxygen. This discovery was almost as exciting as if someone today were to show that iron or copper is composed of two gases chemically combined.

85. Physical properties. Pure water is odorless and tasteless. In thin layers it has no color that can be detected, but it has a bluish tint when observed through considerable thickness. It freezes at 0° and boils at 100° under a pressure of one atmosphere; and the freezing point and the boiling point of water are used as the fixed points in graduating thermometers (see description of thermometers in Appendix B).

When water at 100° is cooled, it steadily contracts until it reaches a temperature of 4°; after that it expands as the temperature falls. A definite volume of water, then, at 4° is heavier than the same volume at any other temperature, and 1 cc. of water at this temperature weighs almost exactly 1 g.; indeed for all practical purposes we may state that *1 cc. of water at 4° weighs 1 g.*

86. Chemical conduct of water. When we say that a certain compound is *stable* we ordinarily mean that it is not easily decomposed by heat. In this sense water is a very stable compound; for when it is heated as high as 25 times its boiling point, only a small percentage of the steam is decomposed, and the resulting hydrogen and oxygen immediately recombine as the steam cools. Water can be decomposed by the electric current (Fig. 17), as well as by certain metals at ordinary temperature and by others at high temperature (§ 60, 1).

Water is a great promoter of many chemical reactions. The presence of even a trace of water is often sufficient to cause two substances to react. Thus we have seen how brilliantly phosphorus burns in oxygen (§ 42); but if the phosphorus and oxygen are both free from even a trace of water, the two will not combine at all. Just why this is so is not definitely known; but we hide our ignorance by saying that the water acts as a catalyst (§ 40).

Many compounds, such as ordinary alum, combine with water, and the resulting compounds are known as *hydrates*. If these hydrates are heated, the water is driven off, and the resulting compounds are said to be *anhydrous*, a word signifying "without water." The water expelled on heating a hydrate is known as *water of hydration,* or sometimes as *water of crystallization,* although the latter term is misleading.

87. Impurities in natural waters and their effect on health. Pure water is never found in nature. The waters of the ocean, of the rivers, and of even the best wells and springs always contain in solution certain gases and mineral matter dissolved from the air, the soil, and the rocks with which these waters come in contact. One liter of the waters of the ocean contains about 40 g. of mineral matter, more than three fourths of which is common salt. River waters contain much less, not more than 0.5 g. per liter.

In addition to gases and mineral matter, most natural waters contain microscopic living organisms (bacteria). This is true especially of waters in densely populated districts where sewage refuse is likely to find its way into the streams; for such refuse not only contains these organisms but it serves as a food for them, and they multiply rapidly in its presence.

The mineral matter in water rarely has any injurious effect on health; indeed, it supplies material for building up the solid tissues of the body, and water with an ordinary mineral content is to be preferred to absolutely pure water. Many of the bacteria are also without injurious effect, and may even serve to purify the water by destroying the food upon which they live. Others, however, are the direct cause of certain diseases. For example, typhoid fever is due to a certain bacterium that gets into the human system chiefly through the drinking-water; and this much-dreaded disease has been largely stamped out by purifying our water supplies (Fig. 42). The appearance of a water is no assurance of its purity. Only the trained chemist and bacteriologist can make tests that are trustworthy.

88. How can natural waters be purified? Pure water is necessary for many purposes. It would not do, for example, to fill up our automobile batteries with natural water, for the mineral matter present would injure them. The chemist especially has need of pure water. To obtain it, he boils the natural water and cools or *condenses* the steam in clean vessels. The process is called *distillation*, and the purified water so obtained, *distilled water*. In this the mineral matter is removed; for it is not volatile and remains in the vessel in which the water is boiled. The process of distillation is usually carried out as shown in Figs. 43 and 44.

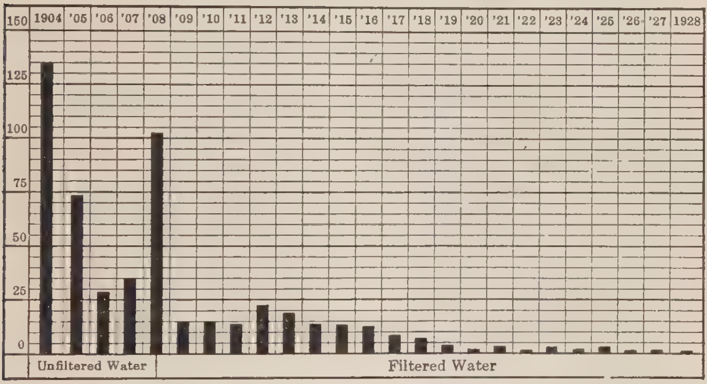


FIG. 42. This chart gives the typhoid fever death rate, over a number of years, per 100,000 of population in Columbus, Ohio, and shows the effect of water purification in decreasing the ravages of this disease

Ordinarily when we speak of pure water, we do not mean water from which *all* impurities have been removed, but simply water that contains nothing injurious to health. Since it is the bacteria present that render water dangerous to health, it is only necessary to destroy these to render the water wholesome. This can be done by distillation, and distilled water is often sold for drinking purposes. The same end can be accomplished by simply boiling the water for a few minutes, for the heat kills bacteria. But plainly these methods cannot be used for purifying the water

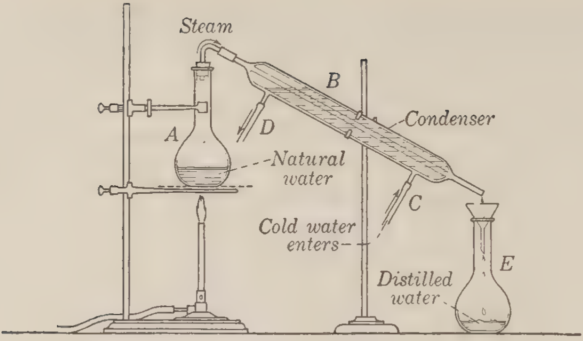

Steam
B
Condenser
A
D
Natural water
C
Cold water enters
E
Distilled water

FIG. 43. Laboratory distillation

Natural water is boiled in the flask A, and the resulting steam is led through the inner tube of the condenser B, which is kept cold by tap water entering at C and flowing out at D. The steam is condensed to liquid form by the cold water surrounding the inner tube and is caught in the receiver E

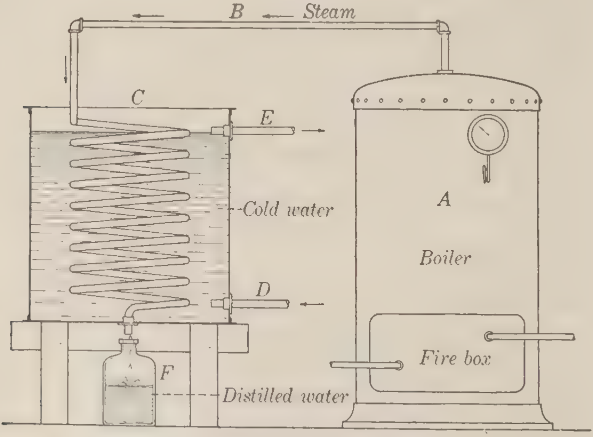
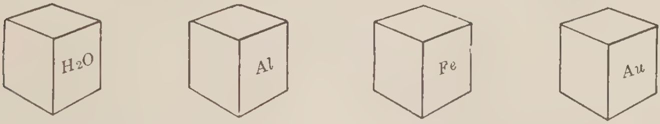

B
Steam
C
E
A
Cold water
Boiler
D
Fire box
F
Distilled water

FIG. 44. Distillation on a large scale

In commercial distillation the natural water is boiled in the large boiler A, and the steam is conducted through B into the condenser C, consisting of a coiled metal tube (usually made of tin) surrounded by cold water supply of a large city. The methods used in purifying such large volumes of water will be reserved for a later chapter (Chap. XL) after the chemical processes employed have been studied.

89. Density. We hear it said that some certain substance is denser than some other substance, as, for example, gold is denser than water. Just what do we mean by the term *density*? *By the density of any substance we mean the weight of it in a unit volume.* When dealing with solids and liquids, we generally use the gram as the unit of weight, and the cubic centimeter as the unit of volume. Adopting these units, *we may define the density of a substance as the weight in grams of 1 cc. of the substance* (Fig. 45).



WATER	ALUMINUM	IRON	GOLD
1 cc. = 1 g. Density = 1	1 cc. = 2.702 g. Density = 2.702	1 cc. = 7.86 g. Density = 7.86	1 cc. = 19.3 g. Density = 19.3

FIG. 45. Densities of some well-known substances

Since 1 cc. of water weighs 1 g., it follows that the number which represents the density of any other solid or liquid also represents its relative weight as compared with water. The term *specific gravity* is often used to represent relative densities using water as the standard; but if we keep to the gram and cubic centimeter as the units of weight and volume, then the number which expresses the density of a substance and that which expresses its specific gravity are identical. In this text we shall adopt the gram and the cubic centimeter as the units of weight and volume respectively, and shall use the word *density* rather than *specific gravity*.

Gases are so light that it is not convenient to define their densities as the weight of 1 cc. We sometimes compare them with air as the unit standard. More often we give the weight of 1 liter of the gas in grams. This number is sometimes referred to as the *liter-density* of the gas. On page facing back cover is given the weight of 1 liter of each of the common gases, and in Appendix E are given the densities of a number of elements.

CHAPTER SUMMARY IN QUESTION FORM

1. Name the two important liquids found in nature.

2. (*a*) Why is water regarded as a compound rather than an element? (*b*) Who first proved it to be a compound?

3. Water is taken as a standard in what measurements?

4. Should you say that 1 cc. of water weighs 1 g. at 0°, at 100°, at 4°, at 75°, or at all temperatures?

5. What word is applied to compounds that are not easily decomposed by heat?

6. Give two ways of decomposing water.

7. Distinguish between the terms *anhydrous* and *hydrates*, giving an example to illustrate.

8. (*a*) What two classes of impurities are found in natural waters? (*b*) What is the effect of each on our health when natural waters are used for drinking?

9. How can we remove all impurities from water?

10. (*a*) Is it necessary to remove all impurities from water in order to make it safe for drinking? (*b*) If not, how can we make it safe for drinking?

11. What word is used to designate the weight of a unit volume of a substance?

THOUGHT QUESTIONS

1. Justify this statement: "The appearance of a water is no assurance of its purity."

2. Compare the meaning of the term *pure water* as used by the chemist with its meaning as used in our homes.

3. How could you determine the total amount of solid matter dissolved in a sample of water?

4. The taste of water is changed by distilling the water, but can be restored by stirring it. Explain.

5. Compare the properties of water with the properties of the elements that compose it.

6. Suppose you wished to determine the amount of water in a tomato; how would you proceed?

7. Why does the chemist use distilled water rather than water that has simply been boiled?

8. Suppose that the maximum density of water was at 0° rather than at 4°; what effect would this have on the formation of ice on lakes and ponds?

9. Water is eight ninths oxygen. Why is it not a good oxidizing agent?

10. Referring to the table in Appendix E, give the weight of 1 cc. of each of the following elements: (*a*) sodium; (*b*) magnesium; (*c*) gold; (*d*) platinum; (*e*) tin.

11. Assuming the densities of alcohol, water, and sulfuric acid to be 0.8, 1, and 1.84 respectively, calculate the weight of each of these liquids required to fill a bottle holding 25 cc.

12. Suppose you had a cube of iron that had a volume of 1000 cc., how large a cube of gold would be required to just balance it on the scales?

FOR HONOR STUDENTS

1. Water collects on the outside of a glass filled with ice water. It collects on the inside of a cold glass inverted over a burning candle. Explain the source of the water in each case.

2. Make a drawing of the apparatus used in your laboratory for obtaining distilled water.

3. Prepare an exhibit of four or five different kinds of food, say an apple, a potato, a tomato, lettuce, flour. Place by the side of each a tube containing the amount of water present in it. (For percentage of water present in each food see table, p. 410.)

CHAPTER VII

THE COMPOSITION OF WATER; HYDROGEN PEROXIDE

The Composition of Water

90. ***Introduction.*** We have already learned that water contains 88.81 per cent oxygen and 11.19 per cent hydrogen by weight. These figures were given in the text, but it is evident that somebody had to determine them before they could be included in the text. The question naturally arises, How can the composition of a compound such as water be determined? In brief the answer is, By experiment. Different methods may be used, but all these belong to one or the other of two general classes, as follows:

1. ***The method of analysis.*** A definite weight of any given compound may be decomposed into its elements, the identity of the elements determined, and also the weight of the amount of each obtained. Let us suppose that we had found a method for separating water into its elements, and that tests showed that these elements were oxygen and hydrogen. We could then start with a definite weight of water, say 100 g., decompose it, and weigh the resulting oxygen and hydrogen. Let us say that the oxygen so obtained weighed 88.81 g. and the hydrogen 11.19 g. Plainly, then, if our work is accurate, the results obtained prove that water is 88.81 per cent oxygen and 11.19 per cent hydrogen. Such a process is called *analysis*. In general, *analysis consists in separating a compound into its elements, or a mixture into its parts.*

2. ***The method of synthesis.*** The method of synthesis is just the opposite of that of analysis; *synthesis consists in determining by experiment the proportion in which the appropriate elements combine to form the compound.* Chemists have found that 88.81 g. of oxygen combine with 11.19 g. of hydrogen to form 100 g. of water. Granting that the work is accurately carried out, these results prove the percentage composition of water.

Which of these two methods is the better adapted for determining the composition of any particular compound must be decided by experiment. It has been found that synthetic methods are best for determining the composition of water. The details of these experiments are very interesting.

91. Synthesis of water by volume. In this method the volumes of hydrogen and oxygen combining to form water are directly measured. In carrying out the experiment we must keep in mind that if we are to compare the volumes of the gases used, we must measure the volumes under the same conditions of temperature and pressure; for the volumes vary with these conditions.

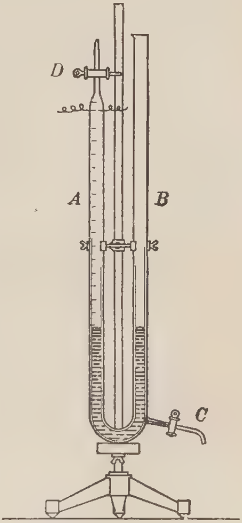


FIG. 46. A convenient form of eudiometer

The combination of the two gases is brought about in a tube called a *eudiometer* (Fig. 46). The two platinum wires fused into the limb *A* of the eudiometer may be connected through a coil to a battery so that an electric spark may be made to pass between the ends of the wires within the tube. The eudiometer is first filled completely with mercury. A few cubic centimeters of pure hydrogen are then admitted to the limb *A* through the stopcock *D*. The stopcock is then closed, and mercury is withdrawn from the stopcock *C*, until the mercury in both limbs of the tube is at the same level and the inclosed hydrogen is at atmospheric pressure. The volume of the hydrogen introduced can then be read off directly on the side of the limb *A*, for this is graduated. Next about an equal volume of oxygen is introduced, the pressure on the gas is adjusted by withdrawing mercury until it stands at the same level in each of the tubes, and the reading is again taken. This reading evidently gives us the total volume of hydrogen and oxygen, and the volume of the oxygen is obtained by subtracting from this the volume of the hydrogen determined above.

The combination of the two gases is now brought about by connecting the battery to the wires, which sends a hot spark through the mixture. Immediately a slight explosion occurs. The mercury in the limb *A* is first depressed, because of the expansion of the gases due to the heat generated in the reaction; but it at once rebounds, taking the place of the gases which have combined to form water. The volume of the water formed is so small that it may be disregarded in the calculation. Mercury is now added to the limb *B* until it stands at the same level in each limb, and the volume of the residual gas in the limb is read off. This gas is then tested to see whether it is oxygen or hydrogen, *since experiment has shown that either the oxygen or the hydrogen will be all used up.* The results obtained enable us to determine the composition of water. From the results of an actual experiment the calculation is made as follows:

1. Volume of hydrogen and oxygen introduced into the tube	40.2 cc.
2. Volume of hydrogen introduced	20.2 cc.
3. Volume of oxygen (difference between volumes 1 and 2)	20.0 cc.
4. Volume of gas (proved to be oxygen) left after explosion	9.9 cc.
5. Volume of oxygen that combined with hydrogen (difference between volumes 3 and 4)	10.1 cc.

Since the gas left after combination had taken place was pure oxygen, then all the hydrogen, 20.2 cc., must have been used to form water. Hence 20.2 cc. of hydrogen combine with 10.1 cc. of oxygen to form water; or, in general terms, *2 volumes of hydrogen combine with 1 volume of oxygen to form water.* Since we know that oxygen is 16 times heavier than hydrogen, we can easily calculate from the above results the proportion *by weight* in which the two gases combine; however, more accurate results can be obtained by direct experiment, as described in § 92.

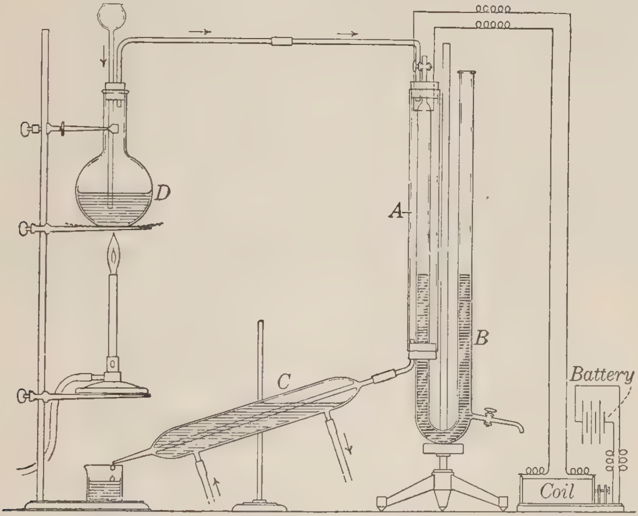


FIG. 47. Apparatus for determining the ratio by volume in which oxygen and hydrogen combine, and the ratio of each of these volumes to the volume of the steam formed

The water formed by the union of measured volumes of oxygen and hydrogen in the eudiometer *B* is kept in the state of gas (steam) by heating a high-boiling liquid in *D* and conducting its hot vapor into the jacket tube *A* surrounding the one branch of *B*. The vapor is then condensed in the condenser *C*

If the limb *A* of the tube is surrounded by steam or the vapor of some liquid with a high boiling point, as shown in Fig. 47, and the experiment is then performed, the water formed remains in the gaseous state (steam). In this way we can compare the volume of the steam formed with that of the hydrogen and the oxygen which combined to form the steam. The results prove that in the experiment just described

$$20.2 \text{ cc. hydrogen} + 10.1 \text{ cc. oxygen} \longrightarrow 20.2 \text{ cc. steam}$$

or

$$2 \text{ volumes of hydrogen} + 1 \text{ volume of oxygen} \longrightarrow 2 \text{ volumes of steam}$$

The important thing to note is that there is a simple ratio between the volumes of hydrogen and oxygen that combine and also between the volume of either one of them and that of the steam formed by their union. We shall have occasion from time to time to refer again to this striking, important fact.

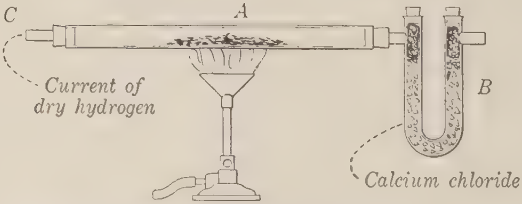


FIG. 48. Apparatus for finding the ratio by weight in which oxygen and hydrogen combine to form water

92. Synthesis of water by weight. This method is based on the fact already noted (§ 64) that hydrogen passed over hot copper oxide takes away oxygen from the oxide and forms water. The oxide is placed in a tube *A* (Fig. 48), and the tube and contents carefully weighed. The tube *B* contains calcium chloride; this tube and its contents are also carefully weighed. The apparatus is then connected as shown in the figure. Heat is now applied to the oxide, and after it is hot a current of *pure, dry* hydrogen is passed into the tube *A* at *C*. The hydrogen combines with the oxygen present in the copper oxide, forming water, which is absorbed by the calcium chloride in the tube *B*. When the copper oxide is reduced, the heat is withdrawn and the apparatus allowed to cool. The tube *A* and contents are again weighed; the loss in weight equals the weight of the oxygen taken from the copper oxide to form water. The tube *B* and contents are also weighed, the increase in weight giving us the weight of the water formed. By subtracting the weight of the oxygen used from the weight of the water formed, the weight of the hydrogen in the water is obtained. The following results of an experiment show the method of calculation:

1. Loss of weight of tube *A* and contents (oxygen used)	2.4 g.
2. Gain in weight of tube *B* and contents (water formed)	2.7 g.
3. Weight of hydrogen present in water formed (difference between weights 1 and 2)	0.3 g.

Hence 0.3 g. of hydrogen combine with 2.4 g. of oxygen to form 2.7 g. of water; or, in whole numbers, 1 part by weight of hydrogen to 8 parts by weight of oxygen.

93. Comparison of results. We have seen that different methods may be used for determining the composition of water. If the methods are accurate, and the experiment carried out with great care, the results will agree closely, but not exactly. The question arises, then, What results are the most reliable? Naturally, the more accurate the method chosen, and the more skillful the experimenter, the more reliable will be the results. All chemists agree that the results obtained for water by the American chemist Morley (Fig. 49) are the most accurate; for not only was Morley a great experimenter, but he devoted a large part of his life to carrying out his experiments. Morley's results show that *water must be regarded as a compound containing hydrogen and oxygen in the ratio of 1 part by weight of hydrogen to 7.94 parts by weight of oxygen; or, expressed in* *percentages, 11.19 per cent of hydrogen and 88.81 per cent of oxygen.*

94. The law of definite composition (the law of definite proportions). We have seen that pure water has a perfectly definite composition. Chemists have found the same to be true of every chemical compound; indeed, *constancy of composition* is the main test used to decide whether or not any given substance is a chemical compound. This important fact is expressed in the *law of definite composition,* which may be stated as follows: *The composition of a given chemical compound is always precisely the same.*

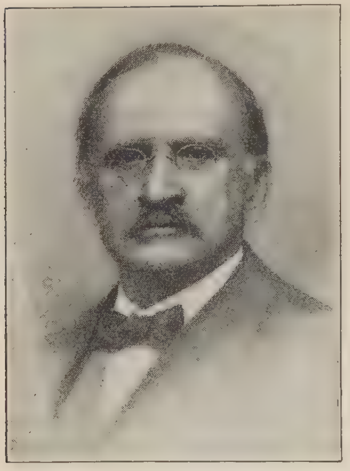


FIG. 49. Edward Williams Morley (1838–1923)

Former Professor of Chemistry in Western Reserve University. Known for his accurate measurements of the densities of oxygen and hydrogen and of the ratio in which they combine to form water

Hydrogen Peroxide

95. General. While the discovery of Cavendish and Lavoisier to the effect that water is a compound of hydrogen and oxygen was of the greatest importance, another one made some forty years later by the French chemist Thénard proved to be of nearly equal interest. Thénard showed that there is a second compound of hydrogen and oxygen which he named *hydrogen peroxide*; and that, although a colorless liquid like water, this new compound differed widely from water in most of its properties and in its chemical conduct. The discovery that the same elements could combine to form more than one compound, while not entirely new, was of great interest, although we now know that this property is characteristic of most pairs of elements; indeed, someone may discover a third compound of hydrogen and oxygen, though this does not seem probable.

96. The composition of water and hydrogen peroxide. While both water and hydrogen peroxide contain only hydrogen and oxygen, the proportions in which these two elements are present are different:

Water contains 1 part of hydrogen to 7.94 parts of oxygen by weight.
Hydrogen peroxide contains 1 part of hydrogen to 15.88 parts of oxygen by weight.

Since water is a very stable compound, it is evident that 1 g. of hydrogen can hold 7.94 g. of oxygen in firm combination. Under very special conditions we can cause the hydrogen to take on a double load of oxygen (2 × 7.94 g., or 15.88 g.), and then we have hydrogen peroxide. However, the hydrogen cannot hold this extra amount of oxygen firmly, so that hydrogen peroxide readily decomposes into water and oxygen; indeed, it is difficult to keep it from doing so.

97. Preparation. Hydrogen peroxide in a pure state is difficult to prepare because it decomposes so easily, and it is even dangerous because its decomposition is often an explosion. The product sold by the druggist contains 3 per cent of hydrogen peroxide and 97 per cent of water. This can be prepared by the action of sulfuric acid on barium peroxide. The reaction may be represented as follows:

$$\underset{\substack{\text{sulfuric}\\\text{acid}}}{H_2SO_4} + \underset{\substack{\text{barium}\\\text{peroxide}}}{BaO_2} \longrightarrow \underset{\substack{\text{barium}\\\text{sulfate}}}{BaSO_4} + \underset{\substack{\text{hydrogen}\\\text{peroxide}}}{H_2O_2}$$

If we examine the above equation, it will be seen that the hydrogen of the acid and the barium of the peroxide have simply changed places. It will be noticed that hydrogen peroxide is represented by the formula H_2O_2 rather than HO. The reason for this will be made clear in due time.

98. Properties and chemical conduct. Pure hydrogen peroxide is a clear, sirupy liquid, much heavier than water (density 1.44). While the pure compound decomposes easily, the dilute solution of the druggist is fairly stable, although it should be kept in a dark, cool place.

99. Uses. Since hydrogen peroxide easily gives up oxygen, it is an excellent oxidizing agent, and most of its uses depend on this property. The stopper of a bottle of the peroxide is usually bleached, and this suggests the use of a solution of the compound as a bleaching agent. Hair and colored cloth of various kinds lose their color when moistened with it, and it has a limited use for this purpose. Its main use is as an antiseptic in medicine, although recent experiments seem to show that it has little value for this purpose.

100. Catalysts (catalytic agents): positive and negative catalysts. We have defined a catalyst (§ 40) as a substance that *changes the speed of a reaction by its mere presence.* Some catalysts increase the speed of a reaction, and this is true of manganese dioxide when used in the preparation of oxygen (§ 40). Such substances are known as *positive catalysts.* Others decrease the speed of the reaction, and these are known as *negative catalysts.* Thus the hydrogen peroxide of the druggist always has in it a trace of some compound, usually the one used in medicine under the name of acetanilide, which acts as a negative catalyst and so preserves the strength of the solution by retarding decomposition of the peroxide. In a general way we might compare the lubricating oil used in an automobile to the action of a positive catalyst, for without undergoing any change itself it enables us to obtain greater speed. The brakes, on the other hand, might be compared to a negative catalyst, for they enable us to decrease the speed.

Catalysts have a most remarkable effect. Suppose you could find a substance which, introduced in small quantities into the waters above Niagara Falls, would either greatly increase the rate of flow of the water over the falls or practically stop it; the action of catalysts is really as wonderful as that would be.

101. The law of multiple proportions. In comparing the composition of water with that of hydrogen peroxide (§ 96), it was pointed out that in water 1 g. of hydrogen is combined with 7.94 g. of oxygen, while in hydrogen peroxide 1 g. of hydrogen is combined with 15.88 g. of oxygen. The significant fact to notice is that the weights of the oxygen combined with 1 g. of hydrogen in the two compounds are in the ratio of 7.94 : 15.88, or 1 : 2. Experiments have shown that results similar to these are obtained whenever *any two* elements combine to form more than one compound; namely, that the weights of the one element combined with a fixed weight of the other element always bear a simple ratio to each other, such as 1 : 2 or 1 : 3 or 2 : 3. This important truth is known as the *law of multiple proportions.* It was formulated by John Dalton (Fig. 57) in 1808, and may be stated thus: *When any two elements, A and B, combine to form more than one compound, the weights of A that combine with 1 g. of B bear the ratio of small whole numbers to each other.*

CHAPTER SUMMARY IN QUESTION FORM

1. Is the composition of a compound determined (*a*) by experiment, or (*b*) by calculation, or (*c*) by both of these processes?

2. (*a*) Name the two general classes of methods used in determining the composition of a compound. (*b*) How do these differ from each other?

3. Which of the two methods named in question 2 serves better for determining the composition of water?

4. Describe somewhat in detail one method for determining the composition of water, and state the results obtained by this method.

5. Many different chemists have determined the composition of water. Their results do not agree exactly. Explain why this is so.

6. (*a*) Give the name of the chemist who is generally regarded as having determined the composition of water with the greatest exactness. (*b*) State his results.

7. (*a*) In what proportion by volume do hydrogen and oxygen combine to form water? (*b*) Suppose that the two gases are mixed in this proportion, then heated to 100° and exploded; how does the volume of steam formed compare with the volumes of the gases that combined to form the steam?

8. (*a*) Name two compounds that are composed of oxygen and hydrogen only. (*b*) How do you account for the fact that we have two entirely different compounds, yet both are composed of the same elements?

9. Contrast the properties of the two compounds referred to in question 8.

10. What do we call (*a*) a substance that by its mere presence increases the speed of a reaction? (*b*) one that similarly decreases the speed of a reaction? (*c*) Give a practical application of each of these two kinds of substances.

11. State two laws of chemical combination illustrated by the compounds water and hydrogen peroxide.

THOUGHT QUESTIONS

1. In determining the composition of water by volume, why must we take into consideration the temperature and pressure of the hydrogen and oxygen?

2. A mixture containing 20 cc. of hydrogen and 10 cc. of oxygen introduced into a tube at ordinary temperatures and exploded would break the tube into pieces. (*a*) Explain. (*b*) Would the explosion be so violent if you had a mixture of, say, 20 cc. of hydrogen and 30 cc. of oxygen?

3. Name the gas that would be left, and state the volume it would occupy, after exploding each of the following mixtures: (*a*) 10 cc. of hydrogen and 15 cc. of oxygen; (*b*) 10 cc. of hydrogen and 5 cc. of oxygen; (*c*) 10 cc. of oxygen and 5 cc. of hydrogen; (*d*) 20 cc. of hydrogen and 20 cc. of oxygen.

4. A chemist determined the composition of water by passing hydrogen over hot copper oxide as explained in the text. He obtained the following results:

Weight of copper oxide and tube before passing hydrogen through	70.6 g.
Weight of copper oxide and tube after passing hydrogen through	64.2 g.
Weight of calcium chloride and tube at beginning of experiment	110.8 g.
Weight of calcium chloride and tube at end of experiment	118.0 g.

Find (*a*) weight of oxygen present in water formed; (*b*) weight of water formed; (*c*) weight of hydrogen in water formed; (*d*) proportion in which the hydrogen and oxygen are present in the water.

5. From the following data determine the ratio in which oxygen and hydrogen unite, the volumes all being measured under the same conditions of temperature and pressure:

Volume of oxygen in eudiometer	4.27 cc.
Volume of oxygen and hydrogen	26.36 cc.
Volume of gas (hydrogen) left after explosion	13.55 cc.

FOR HONOR STUDENTS

1. Prepare the necessary apparatus, and explain to the members of the class just how you would proceed, to determine the composition of water by the action of hydrogen on copper oxide.

2. Write a biographical sketch of Morley. (Consult encyclopedia.)

3. (*a*) What weight of hydrogen is present in 1 kg. of the ordinary hydrogen peroxide of the druggist? (*b*) What weight of oxygen?

CHAPTER VIII

SOLUTIONS

102. *Introduction.* Everyone knows that when salt is stirred in water the white solid completely disappears. What becomes of it? We can get some light on this question by allowing the dish containing the salt and water to stand exposed to the air in a warm place. The water gradually passes off into the air (*evaporates,* § 79) and the white salt is left behind in the dish with just the same properties it had to begin with. It has not been changed into any other substance by the water.

103. Some much-used terms. The chemist expresses the facts just described by saying that the salt *dissolves* in water, and calls the resulting liquid a *solution.* He calls the dissolving liquid (water) the *solvent* and the dissolved substance (salt) the *solute.* He says that salt is *soluble* in water. Most of the compounds with which we shall meet are soluble in water, at least to some extent. Some substances are practically *insoluble,* such as the metals, stones, glass, and cement. Other liquids than water, such as alcohol and gasoline, are also good solvents, especially for such things as fats, oils, and waxes; but water is by far the most general solvent for all classes of substances.

104. All parts of a solution the same. The most striking thing about a well-stirred solution, such as salt dissolved in water, is that every portion of it is just like every other portion — each drop has a salty taste. This fact is expressed by saying that the solution is *homogeneous.*

Since a small weight of salt has been evenly distributed through a relatively large volume of water so that every drop of the solution contains salt, we must conclude that when a solid dissolves it breaks up into extremely small particles, far too small to see or filter out, which become evenly distributed all through the solvent.

We can make this evident to the eye by taking a crystal of an intensely colored dye, no larger than the head of a pin, and dissolving it in a liter of water. *Each drop* of the solution is distinctly colored, though it contains an incredibly small weight of the dye. The dissolved solid has been parted into its molecules (§ 73) just as if it had been changed into a gas.

105. Suspensions. When finely powdered sand or clay (insoluble in water) is well shaken or stirred in water, a milky or muddy-looking (*turbid*) liquid is obtained, called a *suspension*. The solid is not dissolved, and if the mixture stands quietly for a time the solid slowly settles to the bottom of the vessel, leaving the liquid clear. The solid can be removed more rapidly by filtering through filter paper. The solute in a true solution, on the other hand, does not settle, nor can it be filtered out.

106. Chemical solutions. We sometimes say that zinc dissolves in sulfuric acid just as we say salt dissolves in water. The two cases are different, for when we evaporate the salt solution we get back the salt, but when we evaporate the zinc solution we get a white solid, soluble in water, called zinc sulfate. Zinc itself is not soluble either in water or in sulfuric acid. The acid acts chemically on the zinc, changing it into zinc sulfate, which then dissolves. Solutions depending in this way on a preliminary chemical action are called *chemical* solutions.

107. Solutions and compounds. Every sample of a pure compound like sugar is exactly like every other sample *in* *composition,* and every drop of a given solution is exactly like every other drop in composition. Both are homogeneous. How, then, does a solution differ from a compound?

The difference is this: A compound, say sugar, has one fixed composition, and we cannot change this in the least without destroying the compound. A solution of sugar may have *any* proportion of sugar to water up to a certain maximum amount. It is therefore like a mixture rather than like a compound.

If there is little solute present in a solution, we call it a *dilute* solution; if much solute has been dissolved, we call it a *concentrated* solution. Honey is a concentrated solution of sugar; the sap of a maple tree is a dilute solution of sugar.

108. Saturated solutions. If we stir a little salt into, say, 500 cc. of water in a beaker, it will readily dissolve. If we continue to add more salt, a little at a time, we shall presently find that no more salt will dissolve, and we say that the solution is *saturated.* In reality, as can be proved by experiment, some salt particles continue to dissolve, while at the same time an equal weight of salt crystallizes out of the solution, so the concentration of the solution remains unchanged.

We can say that a balance has been reached between the rate at which the salt dissolves and the rate at which it crystallizes from the solution. This balanced state is called an *equilibrium.* When equilibrium has been reached, the net effect is the same as though no changes in solution were taking place. *A solution is said to be saturated* (*at a given temperature*) *when it remains unchanged in concentration while in contact with some of the undissolved solid.*

109. Illustration. The fact that saturation is an *equilibrium* of particles in motion, and not a condition of finished action, may be illustrated by the situation that often occurs at a very popular continuous movie. The seating capacity at first rapidly fills up (the solid rapidly dissolves), then more slowly as seats are difficult to find, until at last all seats are occupied (saturation). A waiting crowd is left over (undissolved solid). Satisfied spectators keep leaving from time to time (crystallize out) and their places are promptly filled from the crowd (excess solid). This is now a state of equilibrium, and will continue as long as a waiting crowd (solid) is present, the seating capacity being always full but with changing individuals. We cannot be sure of complete saturation unless there is a waiting list. If it were possible to add a lot of chairs (corresponding to raising the temperature) there would be a new equilibrium with a larger audience (greater concentration).

110. Solubility. The weight of the solid that will completely saturate a definite weight of a given solvent at a given temperature is called the *solubility* of the solid in that solvent. It is usually defined thus: *The solubility of a solid (at a given temperature) is the weight in grams of the solid that will saturate 100 g. of the solvent.*

111. Supersaturated solutions. A hot solvent usually dissolves much more of a given solid than does the same solvent when cold, and a solvent saturated at a high temperature steadily deposits the excess of the solute in the form of crystals as the temperature falls, keeping saturated all the time. Sometimes the crystals fail to form as the solution cools, especially if no crystals are present when it starts to cool and if it is not disturbed in any way. The solution, when cool, will then contain more of the solute than is normally present at saturation. Such a solution is said to be *supersaturated.* If even a very small crystal of the solute is dropped into a supersaturated solution, the excess of solute at once crystallizes out, leaving the solution saturated.

The fact that supersaturation is an unbalanced state may be shown by tying a thread around a crystal of the solute and lowering it into a supersaturated solution

(Fig. 50). The crystal grows rapidly in size, and fragments, breaking off, start crystallization at other points in the solution. Crystallization goes on until the solution is just saturated. Some jellies are supersaturated solutions, and often deposit the excess of sugar crystals. If heated until all crystals have dissolved and then carefully cooled, supersaturation may be again secured.

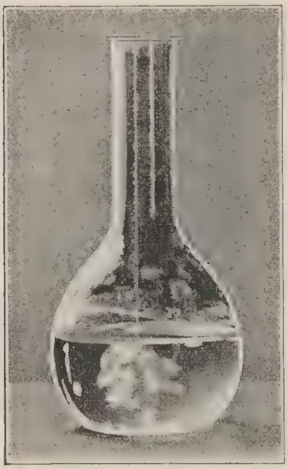


FIG. 50. The rapid growth of a crystal suspended in a supersaturated solution

112. Classes of solutions. There are a number of classes of solutions other than the solution of a solid in a liquid. Every gas freely mixes with every other gas in all proportions, and such a mixture may be thought of as a solution of one gas in another. Gases and solids dissolve in liquids; one liquid often dissolves in another, or in other words the two liquids mix (liquids which will mix are said to be *miscible*); one solid sometimes dissolves in another solid. The most familiar kind of solution is one in which a liquid is the solvent, and a gas, a second liquid, or a solid is the solute.

113. Conditions that affect solubility. The solubility of any given substance depends upon the nature of the solute and of the solvent, and upon both the temperature and the pressure at which the solubility is measured.

1. ***Nature of the solute.*** Each substance has its own peculiar solubility just as it has its own color, taste, or crystalline form. All substances, whether solids, liquids, or gases, may be regarded as being soluble *to some extent* in every liquid; but in many cases the solubility is too small to be measured. No one would think of copper as at all soluble

in water, but it does have a very slight solubility. In other cases the solubility is very great. Some solids dissolve in less than their own weight of water. Alcohol and water mix in all proportions; ammonia gas dissolves to the extent of 1000 volumes in 1 volume of water.

2. ***Nature of the solvent.*** The nature of the solvent is just as individual a matter as that of the solute. Water and alcohol each has its own solvent ability. Water is the most general solvent for all classes of compounds, and alcohol is perhaps next to it. Ether, carbon tetrachloride, and benzene are good solvents for such substances as fats, waxes, and oils; this leads to their use in removing grease spots from clothing.

3. ***Temperature.*** The weight of a substance which a given volume of a solvent can dissolve varies with the temperature. As a rule the solubility of a *solid* increases rapidly as the temperature is raised, so that the boiling liquid dissolves several times the weight soluble in the cold liquid. In some instances, as with common salt and water, the temperature has little effect on solubility. A few solids are more soluble in cold water than in hot water.

With *gases* the effect of temperature is just the opposite. *The lower the temperature of the solvent, the larger the volume of gas which it can dissolve.* By boiling a liquid most gases can be completely driven out of solution; but this is not always true.

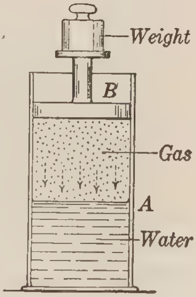


FIG. 51. Henry's law

A gas standing over water in the cylinder *A*, under a pressure that depends upon the weight which is placed on the tight-fitting piston *B*

4. ***Pressure.*** Pressure applied to a saturated solution containing an excess of undissolved solute has little effect upon the solubility of a solid; but when it is applied to a gas standing *over* a liquid (Fig. 51), much more gas is driven into solution. With any given solvent and gas, *the weight of gas going into solution is proportional to the pres-*

sure exerted upon the gas (Henry's law). If the pressure is doubled, the *weight* of gas going into solution is doubled; if the pressure is diminished one half, then but one half as much gas will stay in solution. Under high pressures large quantities of a gas can be dissolved, and when the pressure is removed most of the gas escapes, causing the liquid to foam or *effervesce*. Soda water is a familiar case of a liquid containing a gas under pressure (Fig. 52) — the usual pressure being about ten times the pressure of the atmosphere.

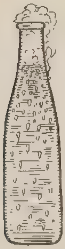


FIG. 52. Soda water

The escape of gas when the stopper is removed

114. Tables of solubilities. For convenience of reference, the facts known about the solubilities of various substances have been collected into *tables of solubilities*, and these are constantly used by the chemist. Solubility curves (Fig. 53) are still more frequently used, since they give the solubility of compounds through a wide range of temperatures. The table below gives the solubility of a number of solids at 0°, 20°, and 100°. A study of this table will show the wide differences in the solubilities of different compounds. For example, at 0° potassium nitrate is only a little more than one third as soluble as sodium chloride, while at 100° it is more than six times as soluble. Calcium sulfate is more soluble in water at 0° than at 100°.

TABLE OF SOLUBILITY OF VARIOUS SOLIDS

SUBSTANCE	WEIGHT DISSOLVED BY 100 G. OF WATER AT		
	0°	20°	100°
Calcium chloride	59.5 g.	74.5 g.	159.0 g.
Sodium chloride	35.70 g.	36.0 g.	39.80 g.
Potassium nitrate	13.30 g.	31.6 g.	246.0 g.
Copper sulfate	14.30 g.	20.7 g.	75.4 g.
Calcium sulfate	0.759 g.	0.203 g.	0.162 g.
Calcium hydroxide	0.185 g.	0.165 g.	0.077 g.

115. Boiling point of solutions. The boiling point of a liquid is *raised* by the presence of a dissolved solid, and for a given solid this raise is proportional to the weight of the dissolved solid. The boiling point of water saturated with a very soluble substance such as potassium nitrate may be raised as much as from 15° to 20° above that of pure water.

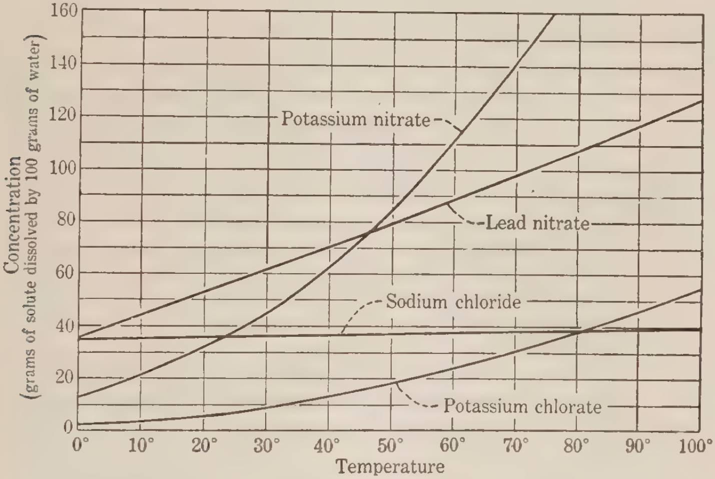


FIG. 53. Solubility represented by means of curves

Increase in temperature is represented in a horizontal direction, and increase in concentration in a vertical direction

116. Freezing point of solutions. The freezing point of a liquid is *lowered* by the presence of a dissolved solute, and (as in the case of the boiling point) for a given solute this lowering is proportional to the weight of solute dissolved. In the case of very soluble compounds this lowering may be as much as from 40° to 50°.

It is for this reason that we put alcohol and similar substances into the radiator of an automobile (Fig. 54), for the water will then not freeze so easily and even at low temperatures will only form a mush of small crystals and never freeze solid. For example, if we use denatured alcohol (about 90 per cent alcohol), the temperature, centigrade and Fahrenheit, at which ice crystals form is as follows:

Percentage by volume of alcohol in water	10	20	30	40	50
Freezing point, centigrade	– 3°	– 7°	– 12°	– 19°	– 28°
Freezing point, Fahrenheit	+ 27°	+ 19°	+ 10°	– 2°	– 18°

117. Deliquescence. All solid bodies tend to adsorb a film of moisture on their surfaces to some degree, and this is described by saying that they are more or less *hygroscopic.* Some very soluble compounds adsorb so much moisture that they become wet to the touch and gradually pass into solution when exposed to moist air. Such substances are said to be *deliquescent.* Calcium chloride, used to dry hydrogen (Fig. 33), is a substance of this kind.

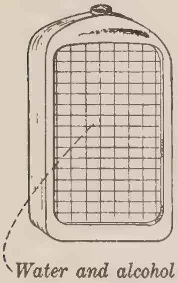


FIG. 54. Protecting the radiator from freezing

118. Efflorescence. We have seen (§ 86) that many solids when crystallized from water form *hydrates,* which are combinations of the compound with water in the form of crystals. Often the water is not very firmly combined with the compound, and when the crystals are exposed to dry air the water is gradually given off as water vapor. The crystals then crumble to powder. Such a compound is said to be *efflorescent* — which word really means "tends to become a powder."

119. Electrolysis of solutions. Pure water does not appreciably conduct the electric current; nor does water in which certain compounds have been dissolved, such as sugar or alcohol. Water, sugar, and alcohol are called *nonelectrolytes.* But if certain other compounds, such as common salt or sulfuric acid, are dissolved in water, the resulting solutions are good conductors. Compounds whose solutions are conductors are called *electrolytes. When the* *electric current passes through a solution of an electrolyte, a chemical change always takes place in the solution.* This change is called *electrolysis.* For example, when the current passes through water containing a small percentage of sulfuric acid, the water is decomposed into oxygen and hydrogen (§ 39, 2).

The general plan used in the electrolysis of a solution is illustrated in Fig. 55. Two plates or rods made of suitable material are connected with the wires from a battery or dynamo, and dipped into the solution as shown in the figure. These plates or rods are called *electrodes.* The electrode connected with the positive pole of the battery is the positive electrode, or *anode*; that connected with the negative pole is the negative electrode, or *cathode.* The particular form of apparatus used varies in individual cases. In the electrolysis of water (Fig. 17) the electrodes are so arranged that the oxygen and hydrogen produced may be collected separately.

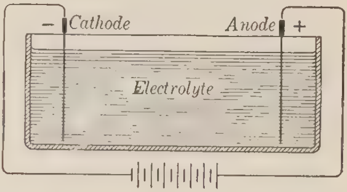


FIG. 55. The electrolysis of a solution of an electrolyte

Since it is clear that *in some way* the electric current passes through the electrolyte from one electrode to the other, it might be expected that chemical action (electrolysis) will be noticed all through the electrolyte. This is not the case. The only visible effect of the current is found at the surfaces of the electrodes. The explanation of this singular fact will be found in a later chapter.

Many of the chemical changes produced by electrolysis are of the greatest importance in the industries. Thus the metal aluminum, so largely used in making automobiles, airships, and cooking vessels, is obtained entirely by electrolysis. By this means also copper is purified, and various objects are plated with gold, silver, nickel, and chromium (electroplating).

CHAPTER SUMMARY IN QUESTION FORM

1. Suppose you stir some salt in water until the salt disappears; what name is given (*a*) to the resulting liquid? (*b*) to the salt? (*c*) to the water?

2. Name some good solvents, and some substances that will dissolve in each.

3. (*a*) Name an important characteristic of a solution. (*b*) What is the distinction between a solution and a suspension?

4. What is the difference between a solution and a compound?

5. Explain what is meant by each of the following terms, and illustrate each by an example: (*a*) dilute solution; (*b*) concentrated solution; (*c*) saturated solution; (*d*) supersaturated solution.

6. What do we mean by the phrase "solubility of a solid in a liquid"?

7. Name the different classes of solutions.

8. Name the different factors that affect the solubility (*a*) of a solid in a liquid; (*b*) of a gas in a liquid.

9. Name (*a*) a compound that is only slightly soluble in water at any temperature; (*b*) one that is much more soluble in hot water than in cold; (*c*) one that is about equally soluble in hot water and in cold; (*d*) one that is more soluble in cold water than in hot (see table, § 114).

10. (*a*) Explain why soda water effervesces. (*b*) What law does this illustrate?

11. What effect has a dissolved solid on (*a*) the boiling point of a liquid? (*b*) the freezing point of a liquid? (*c*) Give a practical application of each of these effects.

12. Give the words that we apply to each of the following compounds: (*a*) one that becomes moist on exposure to air; (*b*) one that attracts so much moisture from the air that it passes into solution; (*c*) one that gives off moisture on exposure to air.

13. Draw a diagram and illustrate by it the meaning of each of the following words: (*a*) electrolyte; (*b*) electrode; (*c*) cathode; (*d*) anode; (*e*) electrolysis.

THOUGHT QUESTIONS

1. How can you tell whether a given solution is (*a*) unsaturated, (*b*) saturated, or (*c*) supersaturated?

2. Since any two samples of a compound have the same composition, and since one drop of a solution has the same composition as any other drop, wherein lies the difference between a compound and a solution?

3. Explain the meaning of the statement "The solubility of sodium chloride at 20° is 36 g."

4. Calcium chloride is used to lay the dust on roads. What property has it that makes it useful for this purpose?

5. Does soda water effervesce when inside the fountain or only when withdrawn?

6. When salt is dissolved in water and the water evaporated, the salt is again obtained in the solid state. If zinc is dissolved in sulfuric acid and the liquid evaporated, not zinc but a white solid is obtained. Explain.

7. By reference to the solubility curves, Fig. 53, determine the solubilities of the following compounds at the temperatures indicated: (*a*) potassium chlorate at 10°, at 50°, at 100°; (*b*) lead nitrate at 30°, at 90°; (*c*) sodium chloride at 10°, at 50°, at 100°.

8. At what temperature is the solubility of potassium nitrate the same as (*a*) that of sodium chloride? (*b*) that of lead nitrate?

9. 100 g. of water at 100° is saturated with potassium chlorate. The resulting solution is reduced to room temperature (20°). What weight of potassium chlorate will be deposited?

FOR HONOR STUDENTS

1. Ordinary household camphor (tincture of camphor) is a solution of the white solid known as "camphor gum" in alcohol. This gum is insoluble in water. Predict what will happen if water is added to the tincture of camphor.

2. Prepare a paper giving the names and statements of all the laws so far studied.

CHAPTER IX

MOLECULES AND ATOMS

Next to the Smallest Things in Chemistry

120. *Introduction.* The industrial chemist spends his life supervising the production of big things — tons of soap, or steel, or fertilizer, or paint. But before he can do this he works out all his plans by picturing to himself the chemical action of things so small that we can hardly imagine them at all. These are *molecules* and *atoms*. In earlier pages both molecules and atoms have been referred to (§§ 73, 29). Can we get a clearer idea about them and why they are so important to the chemist?

121. Molecules. The way gases diminish in volume under increased pressure, expand when heated, and leak through very small holes makes us very sure that matter is made up of extremely small particles. These minute particles we call *molecules* (§ 73). In a gas these molecules are relatively far apart, for we know that a large volume can be compressed into a very small space. Liquids and solids are very little compressible, and so we conclude that their molecules are close together.

To help us realize how small the molecules are, the American chemist Langmuir has calculated that if the molecules in just *one cubic inch of air* were to be each one suddenly changed into a grain of sea sand, the resulting sand would fill a trench three feet deep and a mile wide, extending from New York City to San Francisco. The English physicist Aston gives the following illustration:

Perhaps the most impressive illustration of all is to suppose that you could label the molecules in a tumbler of water. Suppose it was possible to do this in such a way that you would know them again, and you took the tumbler of water and threw it anywhere you please on the earth, and then went away from the earth for a few million years while all the water on the earth, the oceans, rivers, lakes, and clouds had time to mix up perfectly. Now, supposing perfect mixing to have taken place, you come back to earth and draw a similar tumbler of water from the nearest tap, how many of these marked molecules would you expect to find in it? The answer is 2000, for there are that many times more molecules in a tumbler of water than there are tumblers of water on the whole earth.

122. Atoms. Now we have found that water is a *compound,* because from it we can get two different elements, namely, oxygen and hydrogen. Consequently the water *molecule* must be made up of still smaller particles of the elements. These particles of elements that make up molecules of compounds we call *atoms.* The water *molecule* is made up of *atoms* of oxygen and hydrogen.

The molecules of a compound must have the same composition as the compound itself (since it is merely a vast collection of molecules), and this composition is always constant (§ 94). It is therefore evident that the *atoms of a given element* must all have the same weight, or at least the same *average* weight. Otherwise the molecules of the same compound would differ among themselves.

We have stated that matter is made up of molecules. We now see that the molecules in turn are made up of atoms.

123. Molecules and atoms. It is important to distinguish clearly between atoms and molecules. We think of an *atom* as the smallest unit into which an element divides in any chemical action — the grains, so to speak, into which an element can be parted. In general these atoms do not exist independently of each other, but tend to unite in small groups to form *molecules*, and this gives us our great variety of compounds. We may then say:

An atom is the smallest particle of an element that is found as a part of a molecule. A molecule is made up of two or more atoms either of the same kind (molecules of elements) or of different kinds (molecules of compounds).

124. Actual weights of molecules and atoms. Although the molecules are far too small to be seen by the most powerful microscope, it is a wonderful fact that the chemist has found ways *to count the molecules in a given volume of a gas.* Now he can easily weigh this volume of the gas, and if he divides this weight by the number of molecules he has counted *he will have the actual weight of the individual molecules.*

The trouble is that when he has made his calculation it is of little practical value to him, for the weights of molecules are so small — billionths of a milligram — that he can make no use of them. It is as though the sugar merchant were to take the trouble to find out the weight of a single grain of sugar, whereas he always deals in pounds or tons.

Now we can measure the *relative weights* of the various kinds of molecules much more easily than their actual weights, and, as we shall see, we can make many uses of these relative weights. Before explaining how this is done it is important to have clearly in mind just what we mean by relative weights.

125. Meaning of relative values. We are constantly using *relative* values instead of *actual* ones without thinking about it. Our forefathers picked out a stick for measuring and called it a *foot*, dividing it into twelfths called *inches* and multiplying it by three to make a *yard*. The inch and the yard are relative to the foot, and the latter is wholly arbitrary. It might have been any other convenient length, and we should then have had longer or shorter inches and yards.

FIG. 56. Joseph Louis Gay-Lussac (1778–1850)

Distinguished French scientist. He showed the variation of the volume of a gas with its temperature, as did also Charles and Dalton about the same time; determined accurately the ratio by volume in which hydrogen combines with oxygen, as well as the combining ratio of many other pairs of gases, and so formulated the law which bears his name. He made many improvements in analytical processes. He was one of the great teachers of his generation and held a number of public offices, including membership in the House of Peers

FIG. 57. John Dalton (1766–1844)

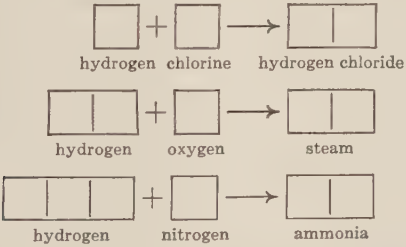
An Englishman famous as a teacher and scientist. He made many studies on the properties and composition of gases (§ 72), but his greatest contribution to science was his development of the atomic theory (§ 136). He wrote an important book entitled "A New System of Chemical Philosophy," which exerted a great influence upon the development of chemistry

FIG. 58. Amedeo Avogadro (1776–1856)

The great Italian scientist who first proposed the theory, now called Avogadro's law, to the effect that equal volumes of all gases contain the same number of molecules

Now we have seen that the actual weights of the molecules are far too small to be of any service to us. Can we get their relative weights and express them in numbers of convenient size to use? To answer this question we must first understand two important laws.

126. Law of combining volumes. When studying the composition of water we found (§ 91) that 2 volumes of hydrogen combine with 1 volume of oxygen to form 2 volumes of steam. It is a surprising fact that these three volumes can all be stated in *whole numbers* without fractions; and we wonder if this just happens to be true in this particular case or whether it is true in other cases as well. Experiment shows that when *any* two gases combine, their volumes, as well as the volume of the product formed (provided it is a gas), can always be stated in small whole numbers. Thus we have



This surprising regularity was first noticed in 1808 by the French chemist Gay-Lussac (Fig. 56), and the following statement of it is called Gay-Lussac's law of volumes: *When two gases combine chemically, there is always a ratio of small whole numbers between the volumes that combine, as well as between the volume of either of them and that of the product (provided it is a gas).*

127. Avogadro's law. The great Italian scholar Avogadro (Fig. 58), born in the year of our Declaration of Independence, was greatly struck by the simple relations stated in the law of volumes, and to explain them he proposed the following theory, now called Avogadro's law: *Equal volumes of all gases contain the same number of molecules, if measured under the same conditions of temperature and pressure.*

Avogadro could not prove his theory to be true, but we now know it is a statement of fact and so call it a *law*. It has been of the greatest service to chemists, for it enables them to measure the relative weights of the molecules.

128. Relative molecular weights. It is easy to weigh a liter each of oxygen, hydrogen, and nitrogen, and these weights are 1.429 g., 0.08987 g., and 1.2506 g. Now these are the weights of *equal volumes* of the three gases, and by Avogadro's law there are the same number of molecules in each of the three liters. Consequently these three numbers, 1.429, 0.08987, and 1.2506, state the *relative* weights of the *three kinds of molecules*, just as the *actual* weights of 100 pennies, 100 nickels, and 100 dimes give us the *relative* weights of the penny, the nickel, and the dime.

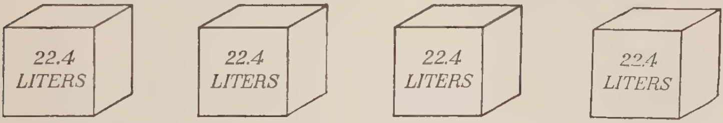
Evidently we can argue the same way about all other gases. So we can conclude that the weights of 1 liter of various gases give us their *relative molecular weights.*

129. Standard for molecular weights. All we now need to do is to decide upon some suitable standard for molecular weights and give it a convenient value — just as we picked out the dollar as a standard in coins and gave it the value 100. Since oxygen is such an important element we very naturally select it as our *standard*, and then begin to consider the most convenient value to give to it.

We can give it the value 1 by dividing the weight of 1 liter of each of the three gases (§ 128) by 1.429. This gives the three relative molecular weights 1, 0.0629, and 0.875. But in general we should like to avoid numbers that are less than unity, just as we have avoided coining half-pennies. So if we put the oxygen molecule 16, we can get the other molecular weights by multiplying the former figures by this number. This gives us 16, 1.008, and 14.01 as our three molecular weights, all of which are greater than unity.

For reasons that will be explained a few pages later, we prefer to make oxygen 32 rather than 16 as our standard value, and this makes the hydrogen molecule 2.016 and the nitrogen molecule 28.02. *Chemists have agreed upon 32 as the standard molecular weight for oxygen in measuring the molecular weights of other gases.*

130. Molecular weights from the weight of 22.4 liters. Having adopted the arbitrary value oxygen = 32 as our standard, let us calculate the volume occupied by 32 g. of oxygen gas. Since 1 liter of oxygen weighs 1.429 g., the volume occupied by 32 g. will be $\frac{32}{1.429}$, or 22.4 liters. If we make a vessel that holds exactly 22.4 liters and fill it with oxygen, it will hold the standard molecular weight (measured in grams), namely, 32 g. (If the vessel is a cube (Fig. 59), each edge will be 28.2 cm. long.) If we now replace the oxygen with nitrogen, the same number of molecules will be present as before (Avogadro's law), and experiment shows that the weight of the nitrogen is 28.02. But these two numbers, 32 and 28.02, are the relative weights of an equal number of molecules, so that the nitrogen molecule weighs 28.02 compared with the oxygen molecule as 32. In like manner the weight of 22.4 liters of *any* gas will give its molecular weight referred to oxygen as 32 (Fig. 59), and we can say that *the number which expresses the weight of 22.4 liters of any gas is the same as the number which expresses the molecular weight of the gas.*



oxygen, 32 g. hydrogen, 2.016 g. nitrogen, 28.02 g. water vapor, 18.016 g.

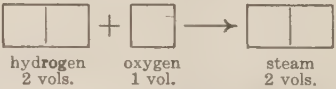
FIG. 59. The weight of 22.4 liters of various gases

So we finally get this general rule: *To find the molecular weight of any gas, find the weight of 22.4 liters of the gas.* The molecular weights so found are not *actual* weights, but are *relative* to oxygen molecules given the convenient value 32. It should be added that the values we get in this way are not *exactly* correct, because no gas *exactly* obeys the laws of gases. Knowing the *approximate* molecular weights, we have other methods for making them exact.

131. Molecular weights of liquids and dissolved solids. Methods similar to the one we have just described for gases have been devised for measuring the molecular weights of certain liquids and of solids in solution. As we shall see later, solid crystals do not have a simple molecular weight, but all the atoms in the crystal are spaced apart in regular order like piles of cannon balls in a military park.

132. Two atoms in the molecule of oxygen. Let us now return to the reason for choosing 32 rather than 16 for the molecular weight of oxygen.

We have found by experiment that when hydrogen and oxygen combine to form steam the volume relations are as follows:



Let us suppose that the 1 volume of oxygen contains 100 molecules. Then the 2 volumes of steam must contain 200 molecules (Avogadro's law). But each of these 200 molecules must contain *at least* one atom of oxygen, or 200 in all, and these 200 atoms came from 100 molecules of oxygen. Therefore each molecule of oxygen must contain *at least* two atoms. Similar reasoning from other reactions shows that the molecule of hydrogen also must contain at least two atoms.

Evidently we have merely shown that there are *at least* two atoms in these molecules. There might be more, but there is no evidence that points this way, and we assume that there are two only. By choosing 32 instead of 16 for the molecular weight of oxygen, the atomic weight of oxygen becomes 16, and the *atomic* weights of all other elements are kept above unity.

133. Relative atomic weights. Having succeeded in finding a method for measuring the relative weights of *molecules*, we want very much to be able to measure the relative weights of the various kinds of *atoms*. This has proved to be a harder problem. But since we are able to measure the relative weights of molecules *made up of atoms*, ways have been found to deduce the atomic weights from the molecular weights. We shall not describe these methods, for they are confusing to the beginner in chemistry. It is sufficient to say that the relative atomic weights have all been measured accurately, and a list of these weights will be found on the inside of the back cover.

134. Molecular weights of elements. If we find the weight of 22.4 liters of a number of gaseous elements, we discover that many of them have molecules made up of two atoms, like hydrogen and oxygen. Molecules of ozone (§ 54) consist of three atoms, and a few elements have still more atoms in their molecules. Others, like mercury, have only one — that is, their vapor is made up of separated atoms.

135. Summary. The meaning of the terms *molecular weight* and *atomic weight* may be summed up as follows:

The molecular weight of an element or of a compound is the relative weight of its molecule compared with the weight of the oxygen molecule, fixed for convenience at 32.

The atomic weight of an element is the relative weight of its atom compared with the weight of the oxygen atom fixed at 16, or of the oxygen molecule fixed at 32.

The chemist depends on molecular weights and atomic weights just as much as the carpenter depends on his foot-rule, or the surveyor on his level. All his calculations are based on them, and we must understand their meaning if we are to make progress in chemistry.

How we came to believe in Atoms

136. The atomic theory. From the time of the early Greeks, four centuries before the beginning of the Christian Era, some philosophers maintained that matter is made up of atoms, or indivisible particles, while others denied that this is so; but there were no proofs either way, so these views were merely speculation with no practical outcome.

More than a century ago (1808) the Englishman John Dalton (Fig. 57) saw that the conduct of gases, and especially the law of constant composition, furnished *proofs* for the first time that matter *acts* as though it were made up of atoms. Chemists eagerly sought for other proofs, and have found so many of them that there is no longer any doubt about the *truth. All forms of matter are made up of atoms.*

137. What atoms are like. Since we cannot *see* atoms, we can only guess what they are like from the way they *act.* Dalton probably thought of them as hard, approximately spherical bodies, much like various sizes of shot; and such an idea was about all that the facts then known justified. Today we have very good reason for believing that an atom resembles our solar system, having a relatively heavy center or *nucleus,* corresponding to the sun, with much lighter satellites, like planets, revolving around the nucleus. Later on we shall learn more about this structure.

138. The scientific method for finding truth. We hear much today about the *scientific method* of getting at the truth about things. Just what do we mean by this? We can get a very good idea of the scientific method by studying more closely the development of the atomic theory.

The Greek speculations accomplished nothing because they were not founded on *any known facts* about how matter acts. They were merely opinions. The first real step was taken when men began to *experiment* on how gases act under varying pressure, and especially when they had *proved* that a given compound has precisely a definite composition. Men then wanted to know the *cause* of this definite composition, and it was John Dalton who clearly *imagined* this cause. He saw that if matter is made up of atoms, each kind having its own definite weight, the law of definite composition would be explained at once.

Thus, if two kinds of atoms, *A* and *B*, have the weights 5 and 10, and it is their habit to combine one atom of *A* with one of *B*, then each molecule of the compound formed will consist of the two elements in the ratio by weight 5 : 10, or 1 : 2. All samples of the compound, made up of such molecules, will have this same ratio of 1 : 2 by weight in composition.

Dalton also predicted that if in a different compound 1 atom of *A* were to combine with 2 atoms of *B*, then the ratio by weight in any molecule (and therefore in any number of molecules) would be 5 : 20 or 1 : 4. He quickly proved this to be true by experiment, and so demonstrated the law of multiple proportion (§ 101) and gave the reason for it.

139. Steps in the scientific method. The scientific method therefore consists of these steps:

First, find some facts or laws that are so interesting or unexpected that they demand an *explanation*.

Second, *imagine* an explanation which, if it were true, would fit the facts in the case. This is called *making a theory*.

Third, devise many experiments to test the truth of this explanation or theory.

Fourth, if the theory is found to fit the facts well, accept it as true until some other facts come to light that show the theory to be defective. A new theory must then be devised to include the new facts.

It has been by this program of work, imagining theories and constantly testing them by experiment, that science has made its wonderful progress.

CHAPTER SUMMARY IN QUESTION FORM

1. State three facts about gases that lead us to believe that matter is made up of small particles (molecules).

2. (*a*) Clearly explain what we mean by the terms *molecules* and *atoms*. (*b*) Give some idea of the size of molecules.

3. (*a*) Explain what is meant by relative weights. (*b*) Why does the chemist deal with relative weights of atoms and molecules rather than with actual weights?

4. State Gay-Lussac's law of combining volumes, and illustrate by an example.

5. (*a*) State Avogadro's law. (*b*) What does this law enable chemists to determine?

6. (*a*) In determining the relative weights of atoms and molecules what standard has been selected by chemists? (*b*) What value is given to this standard? (*c*) Why not use the lightest gaseous element as the standard?

7. To determine the molecular weight of any gas, we have only to determine the weight in grams of how many liters of the gas?

8. (*a*) Give our reasons for believing that the molecule of oxygen is made up of two atoms. (*b*) Are the molecules of all elements likewise composed of two atoms?

9. Give the meaning of the terms *atomic weight* and *molecular weight*.

10. (*a*) Who formulated the atomic theory of matter? (*b*) Is the statement "All matter is made up of atoms" any longer a theory, or has it become an established fact?

11. Explain what is meant by the term *scientific method*, giving the four steps of the method.

THOUGHT QUESTIONS

1. Is it possible to have (*a*) a molecule of an element? (*b*) an atom of a compound?

2. Why do we believe that all the atoms of the same element have the same weight or at least the same average weight?

3. Why do we believe that all the molecules of the same compound are alike?

4. How does the composition of the molecule of an element differ from the composition of the molecule of a compound?

5. What happens to the molecules of water (*a*) when the water is changed into steam? (*b*) when it undergoes electrolysis?

6. Show how our ideas concerning atoms and molecules account for the law of definite proportion and the law of multiple proportion.

7. In a certain school 160 pupils are studying English; 120, history; 80, science; 40, Latin. Find the relative number of pupils in each of these subjects in terms of the number studying Latin. Show how this illustrates atomic weights.

8. Carbon dioxide is one of the gases exhaled from our lungs. Calculate its molecular weight (see table facing back cover for weight of 1 liter).

9. Show that the fact that 2 volumes of hydrogen combine with 1 volume of oxygen to form 2 volumes of steam is in accord with Avogadro's law.

FOR HONOR STUDENTS

1. Name all the chemists so far mentioned in your study, and one contribution made by each to chemistry.

2. Write a brief biographical sketch of John Dalton (consult any encyclopedia).

3. Show that the following results are in accord with two fundamental laws of chemical combination:

	By Analysis	Relative Weights
A sample of carbon monoxide contains	42.9% carbon	1
	57.1% oxygen	$1\frac{1}{3}$
A sample of carbon dioxide contains	27.3% carbon	1
	72.7% oxygen	$2\frac{2}{3}$

CHAPTER X

FORMULAS, EQUATIONS, PROBLEMS

New Meanings for Symbols and Formulas

140. ***Introduction.*** In Chapter II we found that chemists make use of symbols to indicate the atoms of the various elements. We also found that we could put the symbols together in formulas to represent compounds and to give the relative number of atoms in them. Can we now make further uses of symbols and formulas?

141. New meanings for symbols. Having found ways for measuring the relative weights of the atoms, we can add a new meaning to the symbols we have been using. Instead of having the symbol O stand merely for 1 atom of oxygen, we can now say it stands for 1 atom of oxygen *with a relative atomic weight of 16.* In the same way the symbol Hg will stand for 1 atom of mercury with a relative atomic weight of 200.61. From now on the symbol of an element will mean not only 1 atom of the element *but also a definite weight value,* namely, its atomic weight.

142. Formulas represent molecules. We have been using formulas to show merely the kind and relative number of atoms in a *compound.* Now any weighable quantity of a compound is made up of a vast number of molecules, each of which must have the same composition as the compound itself; for every compound has a perfectly constant composition (§ 94). So we shall now use our formulas to represent the *molecule* of the compound, and the symbols in the formula to represent the relative number of *atoms in the molecule.*

Thus the formula H_2O now represents *one molecule* of water, made up of 2 atoms of hydrogen and 1 of oxygen; the formula $KClO_3$ represents one molecule of potassium chlorate, made up of 1 atom of potassium, 1 atom of chlorine, and 3 atoms of oxygen.

Since formulas represent molecules, it follows that we have formulas of elements as well as of compounds. Thus the molecule of hydrogen as well as that of oxygen (§ 132) consists of 2 atoms; hence the formulas of these elements are H_2 and O_2 respectively. There is then a difference between the expression 2 H and H_2; the former represents 2 atoms of hydrogen uncombined, the latter represents the two atoms combined in a molecule.

143. Formulas represent molecular weights. If the symbol of an element represents the *weight of the atom*, then evidently the formula of a molecule (made up of symbols) must represent the *weight of the molecule*. In the formula H_2O the oxygen atom weighs 16 and each hydrogen atom 1.008; so the formula of water, H_2O, represents one molecule weighing 18.016. The formula for potassium chlorate, $KClO_3$, is made up of 1 atom of potassium weighing 39.1, 1 atom of chlorine weighing 35.46, and 3 atoms of oxygen each weighing 16. This gives a total of 122.56. The *molecule* of potassium chlorate therefore weighs 122.56 compared with the oxygen molecule weighing 32 or with the oxygen atom weighing 16.

144. How we get formulas. When we find a new compound, we first analyze it or make it by synthesis, and so get its *percentage* composition, as in the case of water. This we found to consist of 11.19 per cent of hydrogen and 88.81 per cent of oxygen (§ 93); or 11.19 g. of hydrogen and 88.81 g. of oxygen in 100 g. of water.

Now these figures represent *parts in 100* of water; but the chemist wants to know how many *atoms* of each element are present in a *molecule* so that he can represent the compound by a formula. If the number of grams of each element in 100 g. of a compound be divided by the atomic weight of that element (that is, the relative weight of its atoms), the quotients will be *the relative numbers of the several kinds of atoms* in the compound, and so in its molecule. Thus, in the case of water,

Hydrogen: $11.19 \div 1.008$ (at. wt. of hydrogen) $= 11.10$
Oxygen: $88.81 \div 16$ (at. wt. of oxygen) $= 5.55$

This proves that there are *relatively* 11.10 atoms of hydrogen and 5.55 atoms of oxygen in the molecule of water. To get the simplest ratio, we divide each of these numbers by the smaller (5.55) and get the ratio 2 : 1, or 2 atoms of hydrogen to 1 of oxygen.

This tells us that the molecule of water contains twice as many atoms of hydrogen as of oxygen. Evidently the *simplest* formula is H_2O, but other formulas are possible such as H_4O_2, H_6O_3, H_8O_4; all these have twice as many atoms of hydrogen as of oxygen, but each has a different molecular weight, thus:

Formula	**Hydrogen**		**Oxygen**		**Molecular Weight**
H_2O	2×1.008	+	16	=	18.016
H_4O_2	4×1.008	+	2×16	=	36.032
H_6O_3	6×1.008	+	3×16	=	54.048
H_8O_4	8×1.008	+	4×16	=	72.064

Now experiments show that 22.4 liters of steam weigh approximately 18 g., so that the molecular weight of water must be about 18; hence the correct formula for water must be H_2O, since this is the only one of the possible formulas that is in accord with the molecular weight of water as found by experiment.

Let us take another example, namely, the determination of the formula of mercuric oxide. Its percentage composition as found by analysis is mercury 92.6 per cent and oxygen 7.4 per cent. Dividing each of these numbers by the atomic weight of the corresponding element, we have the following results:

Mercury: $92.6 \div 200.6$ (at. wt. of Hg) $= 0.461$
Oxygen: $7.4 \div 16$ (at. wt. of O) $= 0.462$

The ratio of atoms of mercury to oxygen in the molecule of mercuric oxide is therefore 1 : 1, so that the formula for mercuric oxide must be HgO or some multiple of this. Now mercuric oxide is a crystalline solid and so has no simple molecular weight (§ 131). In all such cases we select the simplest formula that the compound could have. Since the simplest possible formula for mercuric oxide is HgO, we adopt this as the formula for the compound.

145. Steps in the determination of formulas. These, then, are the steps in the determination of the formula of a compound: (1) determine the percentage composition of the compound by experiment; (2) calculate from the percentage composition the relative number of the different kinds of atoms present in the molecule, and from this deduce the possible formulas that the compound may have; (3) determine the molecular weight by experiment; (4) calculate which of the possible formulas is the correct one. In case no methods are known for determining the molecular weight of the compound, select the simplest possible formula that the compound can have.

146. Percentage composition from formulas. We determine the formula of a compound from its percentage composition. Having once determined the formula, it is an easy matter to translate the formula back into the percentage composition of the compound.

Example

Zinc sulfate; formula $ZnSO_4$

Zinc, 1 atom	65.38
Sulfur, 1 atom	32.06
Oxygen, 4 atoms	64
Total weight	161.44

Of this total weight, 65.38 parts are zinc, 32.06 parts are sulfur, and 64 parts are oxygen;

65.38/161.44 is zinc; or 40.50%
32.06/161.44 is sulfur; or 19.86%
64/161.44 is oxygen; or 39.64%
Total 100.00%

147. Chemical equations. Having devised a way to express the composition of molecules (and therefore of masses of molecules) by formulas, the chemist goes a step farther and expresses chemical reactions by means of these formulas.

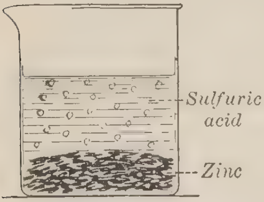


FIG. 60. A beaker in which sulfuric acid is acting upon pieces of zinc

For example, we may imagine a beaker containing pieces of zinc to which sulfuric acid has been added (Fig. 60), producing zinc sulfate and hydrogen. We may summarize this reaction in a word equation, thus:

Word equation:

Zinc + sulfuric acid ⟶ zinc sulfate + hydrogen

But this reaction really takes place between atoms and molecules, for all of which we have formulas. We can write the corresponding *formula* equation thus:

Formula equation: $Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$

We write hydrogen H_2 and not 2 H, because we have found that hydrogen gas consists of molecules, each of which contains 2 atoms (§ 142). Zinc is a solid and we give it the simplest possible formula (§ 144).

148. Balancing the equation. Since chemical formulas indicate not only the elements in the molecule *but the relative weights of the atoms and molecules as well,* every correct equation must balance; that is, it must have as many atoms of each kind on one side of the arrow as on the other side, for a reaction cannot create or destroy an atom (law of conservation of matter, § 13). The equation just given balances as it stands. Many others must be balanced.

When an equation does not balance, it cannot be corrected by changing a formula, for formulas are the result of experiment and express *facts*. An equation is balanced by placing numerals before some of the formulas in it, to indicate the numbers of molecules concerned. The following examples will illustrate how this is done.

Example 1

Let us find the equation for the action of hydrochloric acid on zinc.

Word equation:

Zinc + hydrochloric acid ⟶ zinc chloride + hydrogen

Formula equation: $Zn + HCl \longrightarrow ZnCl_2 + H_2$

Balanced equation: $Zn + 2\ HCl \longrightarrow ZnCl_2 + H_2$

Example 2

Equation for the burning of the metal magnesium in air. Keep in mind that the oxygen molecule, like the hydrogen molecule, consists of 2 atoms, and that magnesium is a solid to which we give the simplest possible formula.

Word equation: Magnesium + oxygen ⟶ magnesium oxide

Formula equation: $Mg + O_2 \longrightarrow MgO$

Balanced equation: $2\ Mg + O_2 \longrightarrow 2\ MgO$

149. Gram-molecular weights; gram-atomic weights. We have learned that the equation

$$\underset{65.38}{Zn} + \underset{98.076}{H_2SO_4} \longrightarrow \underset{161.44}{ZnSO_4} + \underset{2.016}{H_2}$$

tells us that 1 atom of zinc requires 1 molecule of sulfuric acid to complete a reaction that produces 1 molecule of zinc sulfate and 1 molecule of hydrogen.

The weight of the zinc atom and that of the molecule of sulfuric acid are different. These relative weights are placed below the formulas in the above equation. If we want to bring together just the right weights of zinc and of sulfuric acid for the reaction, we must have them in the ratio 65.38 : 98.076, *not* in the ratio of the numbers before the formulas, namely, 1 : 1.

Since the chemist weighs his material in *grams,* we say that we use zinc and sulfuric acid in the proportion 65.38 *grams* of zinc and 98.076 *grams* of sulfuric acid. This gram-weight corresponding to the formula of a substance is called its gram-molecular weight. *The gram-molecular weight of any substance is the weight in grams corresponding to the sum of the atomic weights in its formula.* The gram-molecular weight of sulfuric acid is 98.076 g.; that of water is 18.016 g. Similarly, *the gram-atomic weight of any element is the weight in grams corresponding to the atomic weight of the element.* Thus, 1.008 g. is the gram-atomic weight of hydrogen, and 65.38 g. that of zinc.

150. Problems based on equations. An equation gives an accurate statement in chemical symbols of the relative weights of all materials taking part in a reaction and formed in it. When, by experiment, we have got an equation, we can use it in calculating the *actual* weights of materials used up or formed in the reaction expressed by the equation — yields that are possible from given weights of materials, or weights required to produce desired quantities.

In learning to use equations in this way, it is best to follow a definite order of procedure until through experience you see clearly the steps you can safely omit. The steps are these:

1. Write the word equation.
2. Write the correct formula for each substance involved in the reaction.
3. Balance the formula equation.
4. Under each formula place the formula weight times the coefficient (if any) before the formula.

5. Place the weight (in grams) of the substance named in the problem above its formula, and x above the formula of the substance required.

6. Check the total formula weight on each side of the equation (these are equal; this serves simply to check the accuracy of your figures).

7. Solve for x.

Example 1

How many grams of copper oxide will be formed by heating 60 g. of copper in air?

1. $\text{Copper} + \text{oxygen} \longrightarrow \text{copper oxide}$

2. $Cu + O_2 \longrightarrow CuO$

3. $2\,Cu + O_2 \longrightarrow 2\,CuO$

4 and 5.

$$\overset{60\text{ g.}}{\underset{2 \times 63.57}{2\,Cu}} + \underset{2 \times 16}{O_2} \longrightarrow \overset{x}{\underset{2(63.57 + 16)}{2\,CuO}}$$

Atomic weights

6. $127.14 + 32 = 159.14$

7. $$\frac{60\text{ g.}}{127.14} = \frac{x}{159.14}$$

By clearing of fractions:

$$127.14\,x = 159.14 \times 60\text{ g.}; \text{ or } x = 75.1\text{ g.}$$

Example 2

How many grams of potassium chlorate will be required to yield 100 g. of oxygen?

1. $\text{Potassium chlorate} \longrightarrow \text{potassium chloride} + \text{oxygen}$

2. $KClO_3 \longrightarrow KCl + O_2$

3. $2\,KClO_3 \longrightarrow 2\,KCl + 3\,O_2$

4 and 5.

$$\overset{x}{\underset{2(39.1 + 35.46 + 3 \times 16)}{2\,KClO_3}} \longrightarrow \underset{2(39.1 + 35.46)}{2\,KCl} + \overset{100\text{ g.}}{\underset{3(16 \times 2)}{3\,O_2}}$$

6. $245.12 = 149.12 + 96$

7. $$\frac{x}{245.12} = \frac{100\text{ g.}}{96}$$

By clearing of fractions: $96\,x = 245.12 \times 100\text{ g.}$; or $x = 255.3\text{ g.}$

151. Problems involving volumes of gases. We must remember that the atomic weights used in solving the above problems apply only to *weights* and not to *volumes.* For example, suppose that we desire to calculate the weight of potassium chlorate required to prepare 100 *liters* of oxygen. In solving this problem we must first determine the *weight* of the 100 liters of oxygen; 100 × 1.429 (the weight of 1 liter of oxygen) = 142.9 g. The problem is now restated as follows: What weight of potassium chlorate is required to prepare 142.9 g. of oxygen? We can then proceed as in the above problem.

152. Equations of reactions so far studied. Let us now write the first three steps in making the equations for the reactions so far studied. *Remember that in each case the balanced equation is the correct one.*

Preparation of oxygen. (1) From potassium chlorate.

Word equation:
Potassium chlorate ⟶ potassium chloride + oxygen
Formula equation: $KClO_3 \longrightarrow KCl + O_2$
Balanced equation: $2\ KClO_3 \longrightarrow 2\ KCl + 3\ O_2$

(2) From the electrolysis of water.

Word equation: Water ⟶ hydrogen + oxygen
Formula equation: $H_2O \longrightarrow H_2 + O_2$
Balanced equation: $2\ H_2O \longrightarrow 2\ H_2 + O_2$

Preparation of hydrogen. (1) From sodium and water.

Word equation:
Sodium + water ⟶ sodium hydroxide + hydrogen
Formula equation: $Na + H_2O \longrightarrow NaOH + H_2$
Balanced equation: $2\ Na + 2\ H_2O \longrightarrow 2\ NaOH + H_2$

(2) From zinc and sulfuric acid.

Word equation:
Zinc + sulfuric acid ⟶ zinc sulfate + hydrogen
Formula equation: $Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$
Balanced equation: $Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$

(3) From zinc and hydrochloric acid.

Word equation:

Zinc + hydrochloric acid ⟶ zinc chloride + hydrogen

Formula equation: $Zn + HCl \longrightarrow ZnCl_2 + H_2$

Balanced equation: $Zn + 2\ HCl \longrightarrow ZnCl_2 + H_2$

(4) From iron and steam.

Word equation: Iron + steam ⟶ iron oxide + hydrogen

Formula equation: $Fe + H_2O \longrightarrow Fe_3O_4 + H_2$

Balanced equation: $3\ Fe + 4\ H_2O \longrightarrow Fe_3O_4 + 4\ H_2$

Preparation of hydrogen peroxide. From barium peroxide and sulfuric acid.

Word equation:

Barium peroxide + sulfuric acid
⟶ barium sulfate + hydrogen peroxide

Formula equation: $BaO_2 + H_2SO_4 \longrightarrow BaSO_4 + H_2O_2$

Balanced equation: $BaO_2 + H_2SO_4 \longrightarrow BaSO_4 + H_2O_2$

It will now be clear why we write the formula of hydrogen peroxide H_2O_2 rather than HO. If it were HO, the molecular weight would be 17; if H_2O_2, the molecular weight would be 34. Experiment shows that it really is 34; so the formula H_2O_2 is the correct one.

153. Various meanings of equations. It will be seen that an equation states three kinds of facts and may be read in three ways. The equation

$$Zn + 2\ HCl \longrightarrow ZnCl_2 + H_2$$

states these three facts:

1. *Substance fact:* zinc acts upon hydrochloric acid, forming zinc chloride and hydrogen.

2. *Molecular fact:* 1 atom of zinc acts upon 2 molecules of hydrochloric acid and forms 1 molecule of zinc chloride and 1 molecule of hydrogen.

3. *Weight fact:* 1 gram-atomic weight of zinc (65.38 g.) acts upon 2 gram-molecular weights of hydrochloric acid

(2 × 36.47 g.) to form 1 gram-molecular weight of zinc chloride (136.29 g.) and 1 gram-molecular weight of hydrogen (2.02 g.).

154. Conditions of a reaction not shown by equations. Equations merely state the composition of the substances concerned in the reaction and the weights of each one. They do not tell the conditions under which the reaction will take place. For example, the equation

$$2\ HgO \longrightarrow 2\ Hg + O_2$$

does not tell us that it is necessary to keep heating the mercuric oxide at a moderately high temperature in order to decompose it. The equation

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

in no way indicates that the hydrogen sulfate must be dissolved in water before it will act upon zinc.

It will therefore be necessary to pay close attention to the details of the conditions under which a given reaction occurs, as well as to the statement of the equation itself.

155. Types of reactions. A careful study of the reactions we have had so far will show that they are of four kinds: (1) *combination*, (2) *decomposition*, (3) *simple replacement*, (4) *double replacement*. Nearly all the reactions we shall study belong to one or the other of these four types.

1. ***Reactions of combination.*** Reactions of combination are those in which two elements unite to form a compound. This is illustrated in the formation of water from oxygen and hydrogen:

$$2\ H_2 + O_2 \longrightarrow 2\ H_2O$$

2. ***Reactions of decomposition.*** Reactions of decomposition are those in which a compound breaks down to form other things, either elements or compounds. All the reactions for the preparation of oxygen illustrate decomposition (§ 152).

3. ***Simple replacement.*** In reactions of simple replacement some one element in a compound is replaced by another free element. Thus in all the reactions for the preparation of hydrogen, the hydrogen in the acids or in water is replaced by a metal and the hydrogen is set free:

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

4. ***Double replacement.*** In reactions of double replacement *two* elements in *two different compounds* exchange places. This is illustrated in the preparation of hydrogen peroxide, in which reaction the barium of the oxide and the hydrogen of the acid exchange places:

$$BaO_2 + H_2SO_4 \longrightarrow BaSO_4 + H_2O_2$$

In many chemical reactions, as in the preparation of oxygen and hydrogen, a gas is formed. It is convenient to indicate this by drawing a line just above the formula of the gas, thus:

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + \overline{H_2}$$

In other chemical reactions taking place between compounds in solution, an insoluble compound is formed. Being insoluble, this will separate out, or, as we say, *precipitate.* We may indicate this by drawing a line just beneath the formula of the insoluble compound, thus:

$$H_2SO_4 + BaCl_2 \longrightarrow 2\ HCl + \underline{BaSO_4}$$

CHAPTER SUMMARY IN QUESTION FORM

1. What name is given to the expression that represents the composition of a molecule of a compound or of an element, in terms of the atoms present in it?

2. State what each of the following symbols and formulas represents: O, H, H_2O, Hg, HgO, K, Cl, $KClO_3$.

3. A molecule of sugar contains 12 atoms of carbon, 22 atoms of hydrogen, and 11 atoms of oxygen. Write its formula.

4. State how many atoms of oxygen are present in each of the following: CO_2, 2 CO, Fe_3O_4, 2 $AgNO_3$, 2 P_2O_5.

5. Give the four steps in the determination of the formula of a compound, and illustrate by showing how the formula of water is determined.

6. Knowing the percentage composition and the molecular weight of a compound, you can determine its formula. Suppose, on the other hand, you are given the formula of a compound, can you from this formula determine the percentage composition and molecular weight of the compound?

7. Explain the meaning of the terms *gram-molecular weight* and *gram-atomic weight.*

8. (*a*) Give the gram-atomic weight of oxygen, of zinc, of gold. (*b*) Give the gram-molecular weight of water, of mercuric oxide, of potassium chlorate.

9. Give the steps in writing an equation, using as an illustration the equation representing (*a*) the action of oxygen on copper; (*b*) the action of sulfuric acid on zinc.

10. The simplest formula for hydrogen peroxide is HO. Why, then, do we give it the formula H_2O_2?

11. Give three kinds of facts that an equation states and one fact that it does not state in reference to a chemical reaction.

12. (*a*) Into how many groups may reactions be divided? (*b*) Give an example to illustrate each group or type.

13. (*a*) Determine the percentage composition of hydrogen sulfate (H_2SO_4). (*b*) How do your results compare with those given in the text in § 60, 2?

14. Suppose you wish 100 g. of hydrogen. (*a*) What weight of hydrogen sulfate will be required? (*b*) How many grams of zinc will be used to set free the hydrogen from the hydrogen sulfate? (*c*) What volume will the 100 g. of hydrogen have under standard conditions?

THOUGHT QUESTIONS

1. Does a formula tell us anything that someone did not have to find out by experiments before the formula could be determined?

2. Write in a vertical column the formulas for the compounds having the following composition: (*a*) 2 atoms of hydrogen, 1 of sulfur, and 4 of oxygen; (*b*) 1 atom of mercury and 1 of oxygen;

(*c*) 1 atom of carbon and 2 of oxygen; (*d*) 2 atoms of iron and 3 of oxygen; (*e*) 2 atoms of carbon, 6 of hydrogen, and 1 of oxygen.

3. Opposite each formula of question 2 write (*a*) the total number of atoms present in the molecule; (*b*) the molecular weight of each compound.

4. Find the percentage composition of each of the following compounds: (*a*) H_2O_2; (*b*) $KClO_3$; (*c*) $ZnSO_4$.

5. Copy the following table and fill in the blank spaces:

PERCENTAGE COMPOSITION OF COMPOUND		RELATIVE NUMBER OF ATOMS IN THE MOLECULE	SIMPLEST RATIO	SIMPLEST FORMULA
Hydrogen	2.76%			
Chlorine	97.24%			
Sodium	39.34%			
Chlorine	60.65%			
Potassium	38.69%			
Nitrogen	13.88%			
Oxygen	47.45%			

6. A compound was found on analysis to contain 5.93 per cent of hydrogen and 94.07 per cent of oxygen. Experiments proved its molecular weight to be approximately 34. Calculate (*a*) its simplest formula and (*b*) its correct formula.

7. The simplest formula of a compound calculated from its percentage composition is CH. Its molecular weight is found to be 78. Find the correct formula.

8. (*a*) Calculate the per cent of carbon and of hydrogen in the compound referred to in problem 7. (*b*) Would the per cent of carbon and hydrogen in the simplest formula be the same as in the correct formula?

9. Balance the following equations:

$Hg + O_2 \longrightarrow HgO$

$H_2 + O_2 \longrightarrow H_2O$

$Zn + HCl \longrightarrow ZnCl_2 + H_2$

$Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2$

$Na + HCl \longrightarrow NaCl + H_2$

10. Clearly indicating each of the seven steps given on page 126, calculate the number of grams of hydrogen that can be set free by the action of 46 g. of sodium on water.

FOR HONOR STUDENTS

1. Acetylene, on analysis, is found to contain 7.7 per cent of hydrogen and 92.3 per cent of carbon; and 1 liter of the gas weighs 1.1621 g. Calculate its formula.

2. Ordinary alcohol has the following composition: carbon, 52.12 per cent; hydrogen, 13.13 per cent; oxygen, 34.74 per cent. Its molecular weight is approximately 46. (*a*) Calculate its simplest formula. (*b*) Calculate its correct formula.

3. Is there any difference between 2 H and H_2? between 2 HCl and H_2Cl_2?

4. Write the formula for ozone (see § 134).

5. In order to study the properties of oxygen, a student wished to prepare four bottles of the gas, each bottle holding 250 cc. To be certain that he would have sufficient gas he decided to prepare five bottles of it. Supposing that under the conditions in the laboratory 1 liter of oxygen weighs 1.4 g., what weight of potassium chlorate would the student require?

6. A student added sufficient sulfuric acid to 50 g. of zinc to dissolve the zinc. He then evaporated the resulting liquid to dryness. Calculate (*a*) the weight of hydrogen evolved; (*b*) the volume of hydrogen evolved; (*c*) the weight of the residue left after evaporation (zinc sulfate is a nonvolatile solid).

CHAPTER XI

CARBON

As Diamond a Costly Luxury; as Coal a Cheap Necessity

156. ***Introduction.*** The word *carbon* is more or less familiar to everyone. It suggests coal and smoke and troubles with automobile engines. In the cities, especially, it annoys us by soiling our clothes. Not so many persons, however, realize that this soft black substance which is so useful as a fuel has also its decorative value, for it is the same substance that composes the very hard, brilliant gem prized for centuries and known as the *diamond.* Carbon also occurs in other forms, and before studying its properties we must first learn what some of these are.

157. Occurrence. In the uncombined state carbon is found in nature in several forms. The *diamond* is practically pure carbon, while *graphite* and the various forms of *coal* all contain more or less free carbon. The element also occurs abundantly in compounds. Carbon dioxide, which we breathe from our lungs, is its most familiar gaseous compound. Natural gas, with which in some parts of the United States we heat our houses, and gasoline, with which we run our automobiles, are largely compounds of carbon and hydrogen. It is a constituent of limestone, as well as of many other rocks. Our foods and our bodies contain large percentages of compounds of carbon (see table, p. 410). More than half the compounds that exist are compounds of carbon. In the free state carbon occurs in both the *crystalline* and the *amorphous,* or noncrystalline, form.

158. Crystalline carbon. Crystalline carbon occurs in two forms, *diamond* and *graphite.*

1. ***Diamond.*** Most of the world's diamonds now come from the mines of South Africa. The crystals as found are usually covered with a rough coating. In order to bring out the brilliancy of the gem, the natural crystals are cut to secure the maximum reflection of light. The cutting of diamonds requires great skill, and is carried on very extensively in Holland and Belgium.

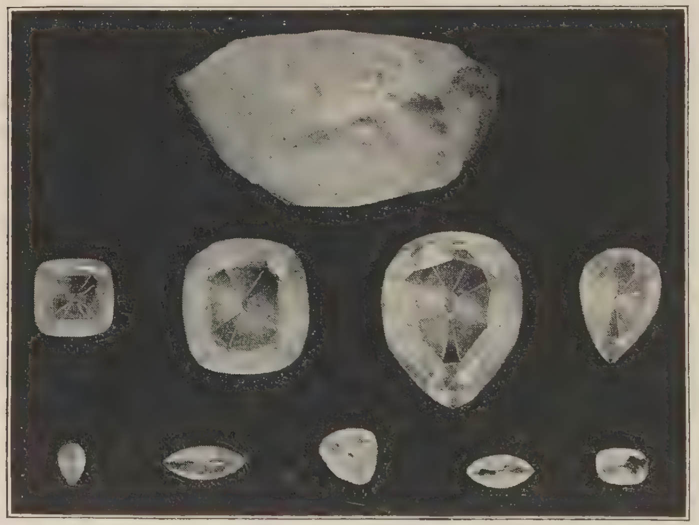


FIG. 61. The Cullinan diamond as originally found, together with the principal stones cut from it (one half natural size)

The weight of the diamond is expressed in *carats*, a carat being equal to about 0.2 g. The word *carat* means the seed, or bean, of the carob tree. These beans may have been used formerly in weighing diamonds.

The largest of all known diamonds is the Cullinan diamond, which was found in South Africa in 1905. The uncut stone weighed $3025\frac{3}{4}$ carats (Fig. 61). Dark-colored diamonds, although of no value as gems, are used to point drills for cutting hard rocks.

The density of the diamond is 3.5, and, though brittle, it is one of the hardest of substances. Few chemical reagents have any action on it; but when strongly heated in oxygen or the air it blackens and burns, forming carbon dioxide:

$$C + O_2 \longrightarrow CO_2$$

Preparation of artificial diamonds. It is natural that chemists should try to make diamonds in the laboratory by crystallizing carbon. For a long time these attempts ended in failure, since graphite, and not diamonds, was always formed. Finally in 1893 Moissan, a famous French chemist, succeeded in producing real diamonds, although they were too small to have any value as gems. He got them by dissolving carbon in melted iron, and plunging the crucible containing the solution into water as shown in Fig. 62. Under these conditions the carbon crystallized in the iron in the form of diamonds. The iron was then dissolved in hydrochloric acid, and little diamonds were found in the insoluble residue.

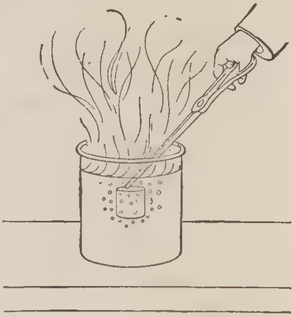


FIG. 62. A drawing illustrating Moissan's method of producing diamonds in the laboratory

2. ***Graphite.*** This variety of carbon is found in large quantities, especially in Ceylon, Siberia, and in some parts of the United States, Mexico, and Canada. Large quantities are also made commercially by heating hard coal to a high temperature (Fig. 63). It is a shining black substance, very soft, and greasy to the touch. Its density is about 2.25. It is used in the manufacture of lead pencils and crucibles, as a lubricant, and (in the form of a polish or a paint) as a protective covering for iron (stove polish).

159. Amorphous carbon. Pure amorphous carbon is best prepared by heating sugar ($C_{12}H_{22}O_{11}$) in the absence of air. The hydrogen and oxygen of the sugar are driven off, largely in the form of water, and pure carbon remains. Almost any form of organic matter yields carbon when heated in the absence of air. Among the numerous substances that contain uncrystallized carbon, the following may be mentioned:

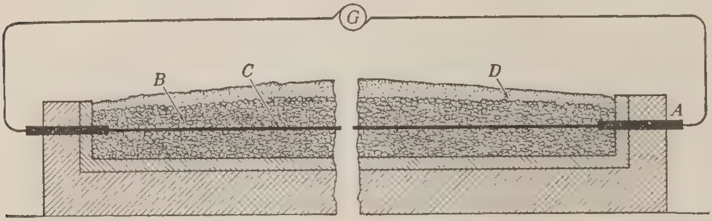


FIG. 63. Electric furnace for the commercial production of graphite

The process consists in heating hard coal in large electric furnaces about 40 ft. in length, a longitudinal section of one of which is here shown. The electrodes *A* are made of graphite. The furnace is nearly filled with the coarse grains of coal *B*. Since the coal is a poor conductor of electricity, there is placed in the center of the charge a core, *C*, of carbon, which serves to carry the current through the charge. The charge is covered with a mixture, *D*, of sand and carbon (or similar materials), which serves to exclude the air. An electric current is supplied by the generator *G*. The current in passing through the charge meets with resistance sufficient to produce a high temperature. Under the influence of the intense heat the carbon is changed into graphite. Prepared in this way, the product is uniform in composition and free from grit and is therefore superior to the natural product for most purposes

1. ***Coal and coke.*** The various forms of coal (Fig. 64) were formed from vast accumulations of vegetable matter. In *hard* coal, or *anthracite*, nearly all the carbon present is in the uncombined state; in *soft*, or *bituminous*, coal a considerable part of the carbon present is combined with hydrogen, oxygen, nitrogen, and sulfur.

When soft coal is heated in the absence of air, there occur complex changes, which result in the formation of various useful compounds of carbon. These compounds are given off in the form of gases and vapors, while the mineral matter and free carbon remain as a solid. This process of decomposition in the absence of air is called *destructive distillation* as distinguished from ordinary distillation (§ 88), which does not bring about chemical changes.

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FIG. 64. Mining coal in a typical mine

The matter which escapes in the destructive distillation of coal is called *volatile* matter; the solid that remains is *coke.* In hard coal the volatile matter averages from 5 per cent to 8 per cent, while in soft coal it averages from 30 per cent to 35 per cent. When coal is burned, the mineral matter present is left in the form of *ash.*

2. ***Charcoal.*** This is prepared from wood just as coke is prepared from coal. The volatile matter formed and expelled by the heat contains many valuable substances, such as *methanol* (wood alcohol) and *acetic acid,* which are obtained commercially in this way. Formerly much of this volatile matter was allowed to escape; but at present a large amount of charcoal is prepared in such a way that

the volatile matter is condensed and saved (Fig. 65), as in the heating of coal for making coke. Both charcoal and coke are used as fuels, and are especially useful in the reduction of metals from their oxides, as will be explained later.

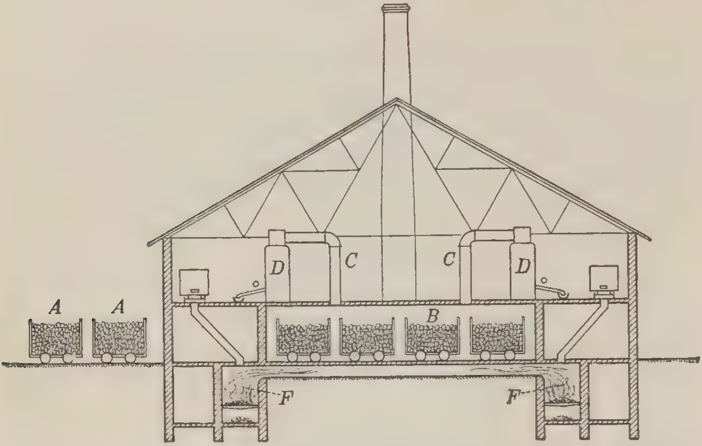


FIG. 65. Drawing of a plant for the production of charcoal by the modern method

Iron cars are loaded with wood A, A and run into a low, narrow iron room, or *retort*, B. The retort is then made air-tight and heated slowly for twenty-four hours by the fires F, F. The volatile products escape through the pipes C, C and then pass into the condensers D, D. Here those portions which are liquid at ordinary temperatures, such as *wood alcohol* and *acetic acid*, are condensed, while the gaseous products are led back and burned in the fires F, F. When all the volatile matter has been expelled in this way, the cars containing the charcoal are run into cooling chambers, and their place in the retort is taken by other cars loaded with wood

3. ***Boneblack, or animal charcoal.*** This is made by charring bones and animal refuse. It consists of calcium phosphate and very finely divided carbon, and is especially useful for removing coloring matter in the refining of sugar.

4. ***Carbon black; lampblack.*** Natural gas and fuel oils are both composed largely of compounds of carbon. When these are burned in a limited supply of air, and the flame is cooled by allowing it to strike against a cold surface, a

part of the carbon of the compounds is set free and collects on the surface. In this or some similar way carbon, together with some impurities, is obtained in the form of a black powder, known as carbon black or lampblack, according to its method of preparation. Large quantities of carbon black are produced (Fig. 66), most of which is used in making automobile tires.

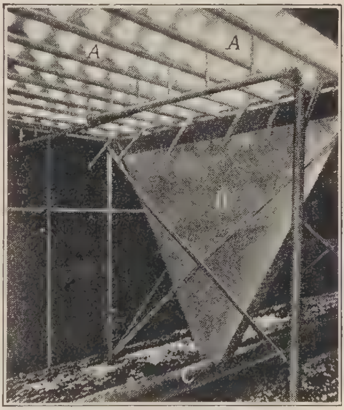


FIG. 66. Making carbon black by the partial burning of natural gas

The flames *A* strike against a cold metal plate. The unburned carbon deposited on this plate is scraped into the compartment *B* and drawn by an air current into the tube *C*, which leads to storage containers

160. Physical properties of carbon. While the various forms of carbon differ in many properties, especially in hardness, yet they are all odorless, tasteless solids, insoluble in water. Even when subjected to the intense heat of the electric arc, carbon does not melt, though it vaporizes to some extent.

In the form of boneblack carbon withdraws certain kinds of organic matter from solutions; hence its use in refining sugar and other substances. A marked property of carbon is its ability to take up (or, in chemical terms, to *adsorb*) large volumes of gases. The amount of gas adsorbed by any given sample of carbon depends not only on the material from which the carbon is prepared but also on the method of preparation. That prepared from coconut shells and peach stones is one of the best for this purpose. For example, 1 volume of charcoal prepared from coconut shells will adsorb about 250 volumes of air. Charcoal prepared especially for adsorbing gases is known as *activated charcoal.*

161. Chemical conduct. At ordinary temperatures carbon is a very inactive substance, but at higher temperatures it combines directly with most of the elements. Because of its strong affinity for oxygen it is an excellent reducing agent. Its compounds with the metals are called *carbides*. One of the most important of these is *calcium carbide* (CaC_2), which is used in the preparation of acetylene. When carbon (or a substance containing it, such as wood or coal) burns, the element combines with oxygen to form either *carbon dioxide* (CO_2) or *carbon monoxide* (CO). Both of these oxides are colorless gases.

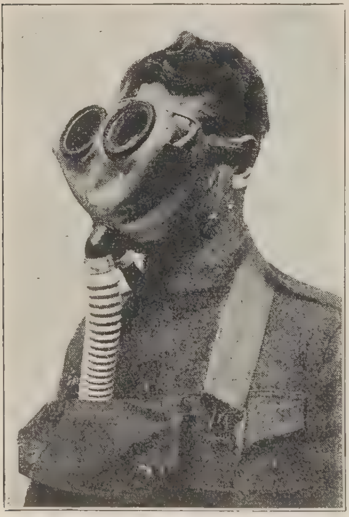


FIG. 67. This form of gas mask, charged with activated carbon, was used in the World War as a protection against poison gas

162. Uses of carbon; summary. The chief use of amorphous carbon is for fuel to furnish heat and power for all the uses of civilization. An enormous quantity of carbon in the form of coal, coke, and charcoal is used as a reducing agent in the separation of the various metals from their ores. Carbon black is used for making motor-car tires, indelible ink, printer's ink, paints, and black varnishes, while boneblack and charcoal are used in filters. Activated charcoal is used in refining various products and in making gas masks (Fig. 67). These masks were developed during the World War to protect the troops from poisonous gases, but are proving useful also for protecting workmen in certain industries from the effects of poisonous gas evolved in industrial operations.

CHAPTER SUMMARY IN QUESTION FORM

1. Mention five different substances that are pure carbon or contain free carbon.

2. (*a*) Which of the substances given in answer to question 1 are crystalline? (*b*) Which contain the most free carbon?

3. Name some of the common compounds of carbon that occur in nature.

4. How do the diamond and graphite differ in (*a*) color? (*b*) density? (*c*) hardness? (*d*) uses?

5. (*a*) Who first prepared diamonds in the laboratory? (*b*) Describe the process.

6. Draw a diagram of an electric furnace and show how graphite is produced in such a furnace.

7. Mention (*a*) three physical properties which are common to all the forms of carbon and (*b*) one in which there is a wide variation.

8. (*a*) What forms of carbon are found in nature? (*b*) What forms are produced in the laboratory? (*c*) What forms are both found in nature and produced in the laboratory?

9. Explain what is meant when we say that coke is prepared by the destructive distillation of coal.

10. Describe the preparation of (*a*) coke; (*b*) carbon black.

11. In making charcoal, name two products obtained in addition to the charcoal.

12. (*a*) What property of carbon makes it useful in gas masks? (*b*) Name the commercial form of carbon that possesses this property to a marked degree.

13. (*a*) Name some of the elements with which carbon combines; (*b*) also name the products formed in each case.

14. Give various uses of each form of carbon.

THOUGHT QUESTIONS

1. Why do we speak of carbon as inactive, when it combines with most of the elements?

2. Both carbon and hydrogen have what important property?

3. (*a*) What is the "lead" used in making lead pencils? (*b*) Why is it called lead?

4. What proof have we that such widely different substances as the diamond, graphite, and anthracite coal are all forms of carbon?

5. Which of the forms of carbon would give the least per cent of ash?

6. Many of the so-called "diamonds" are simply cut glass. Suggest a way of telling these from real diamonds.

7. Prepare a table giving the facts regarding each of the principal forms of carbon, under the following heads:

NAME OF FORM	SOURCE	COLOR	USE

8. If you drop some sugar on a hot stove, the sugar turns black and finally disappears. Explain.

9. When certain kinds of wood are heated in the absence of air, methanol (wood alcohol) (CH_4O) is obtained. (*a*) Does this prove that this alcohol is present in the wood? (*b*) If not, account for its formation.

10. 1 g. of coal on combustion gave 2.9 g. of carbon dioxide (CO_2). (*a*) Calculate the weight of carbon present in the 2.9 g. of the dioxide. (*b*) Calculate the percentage of carbon in the sample of coal burned.

FOR HONOR STUDENTS

1. Design a "carbon tree" in which the trunk is carbon, the main limbs are the different forms of carbon, and the products formed by their combustion are the secondary limbs.

2. Ordinary sugar has the formula $C_{12}H_{22}O_{11}$. Determine the weight of carbon in 1 lb. of sugar.

3. Build and exhibit to the class a model of a furnace for making graphite. The following is listed as suggested material, since it is easily secured: empty chalk box; two crayons; pieces of coal; core of a lead pencil; sand.

CHAPTER XII

THE TWO OXIDES OF CARBON

The One puts out Fire; the Other Burns

163. ***Introduction.*** We have seen that one of the marked properties of carbon is its affinity for oxygen. Whenever carbon is burned in air or in oxygen at ordinary temperatures, carbon dioxide (CO_2) is formed:

$$C + O_2 \longrightarrow CO_2$$

If the temperature is very high and the carbon dioxide comes into contact with very hot carbon, as it will do in passing through a deep bed of hot coals, it combines with more carbon and forms carbon monoxide, as follows:

$$CO_2 + C \longrightarrow 2\,CO$$

Both of these oxides are colorless gases and are of great importance. The dioxide is the more familiar to us, for we are constantly exhaling it from our lungs, and we drink a solution of it in water whenever we take a glass of soda water. The monoxide, on the other hand, is very poisonous, and many deaths result from inhaling it, so that we shall want to learn all about it.

Carbon Dioxide

164. Carbon dioxide (carbonic acid gas) (CO_2). Carbon dioxide is often known as *carbonic acid gas.* It is a colorless and nearly odorless gas and is formed whenever carbon itself or any of the common fuels (all of which contain carbon) burn in oxygen or air. It is also formed in certain processes such as fermentation and the decay of organic matter. Large quantities also escape from volcanoes and crevices in the earth. It is present in the open air to the extent of about 3 parts in 10,000. When we study the atmosphere we shall see that this relatively small amount is essential to the life of all plants; hence it indirectly serves to supply us with our food.

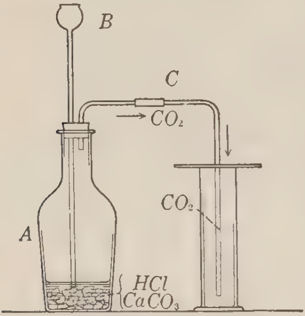


FIG. 68. Preparation of carbon dioxide from calcium carbonate and hydrochloric acid

165. Preparation. In the laboratory carbon dioxide is prepared by the action of hydrochloric acid on the compound known as calcium carbonate ($CaCO_3$). The latter is found in nature in many different substances, such as shells, coral, and limestone. Marble is nearly pure calcium carbonate, and is the material most often used in the preparation of carbon dioxide. When hydrochloric acid and marble are brought in contact with each other (Fig. 68), calcium chloride ($CaCl_2$), water, and carbon dioxide are formed according to the following equation:

$$CaCO_3 + 2\ HCl \longrightarrow CaCl_2 + H_2O + \overline{CO_2}$$

With sulfuric acid the products are calcium sulfate ($CaSO_4$), water, and carbon dioxide.

On a large scale carbon dioxide is prepared by burning coal or coke and separating the resulting carbon dioxide from the other gases formed in the combustion of the fuel. The pure carbon dioxide is then pumped into strong steel cylinders and in this form is sold on the market.

166. Properties. Carbon dioxide is a heavy gas, being about 1.5 times as heavy as air. Because of its weight, it can be poured like water from one vessel into another (Fig. 69). It sometimes escapes from crevices in the earth more rapidly than it can diffuse into the atmosphere, and so has a tendency to collect in deep wells or fissures in the ground. Under ordinary conditions of temperature and pressure (15° and a pressure of 1 atmosphere), 1 volume of water dissolves about 1 volume of the gas. With increasing pressure correspondingly larger volumes of the gas are dissolved (§ 113, 4), and if the pressure on such saturated solutions is withdrawn, most of the gas escapes with effervescence, as in the case of soda water. Carbon dioxide is not regarded as a poisonous gas; however, a high percentage in the air is known to be injurious or even fatal in its effects.

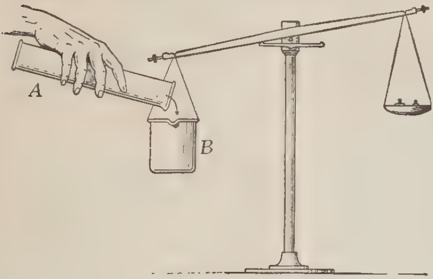


FIG. 69. A method for showing that carbon dioxide is a heavy gas

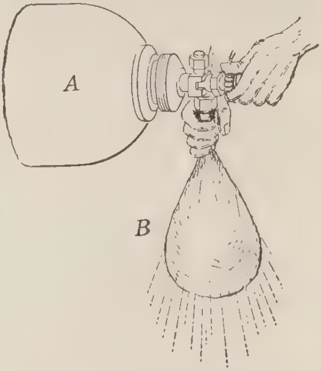


FIG. 70. Liquid carbon dioxide from the cylinder *A* running into the loose bag *B* and evaporating so fast as to leave solid carbon dioxide in the bag

167. Liquid and solid carbon dioxide. When carbon dioxide is forced into a strong vessel at ordinary temperatures until the pressure reaches 52 atmospheres, any additional gas condenses to a colorless liquid. If the pressure on this liquid is suddenly removed (Fig. 70), the liquid then evaporates very rapidly, and the heat absorbed in the process (§ 81) is so great that a portion of the liquid is frozen into a white solid resembling snow. This "snow" slowly evaporates without melting, keeping at a temperature of about −72° as long as it lasts. Solid carbon dioxide is now produced in quantities and sold on the market as "dry ice" (Fig. 71). It has the properties of a good refrigerant, and is coming into large use in shipping ice cream and perishable foods.

FIG. 71. Cutting solid carbon dioxide for commercial use

168. Chemical conduct. Carbon dioxide is neither combustible nor is it a supporter of combustion. When it is passed into a clear solution of calcium hydroxide ($Ca(OH)_2$) (ordinary *limewater*), the solution soon becomes cloudy, owing to the formation of calcium carbonate. The calcium carbonate ($CaCO_3$) is insoluble and separates as a solid as fast as it is formed, producing a cloudy or milky appearance in the solution:

$$Ca(OH)_2 + CO_2 \longrightarrow \underline{CaCO_3} + H_2O$$

This reaction with calcium hydroxide constitutes a simple test for carbon dioxide.

When passed into water a small percentage of the gas unites with the water, forming a very unstable compound, H_2CO_3, known as *carbonic acid*:

$$H_2O + CO_2 \longrightarrow H_2CO_3$$

169. Uses. The carbon dioxide in the air is a food for plants, as will be shown in the chapter on the atmosphere. Commercially it is used chiefly in the manufacture of soda water and like beverages, and in making "dry ice" and certain compounds of carbon. This gas is generated in one form of fire extinguisher. A burning candle is extinguished in air which contains as little as 2.5 per cent of carbon dioxide.

170. Portable fire extinguishers. There are several types of portable fire extinguishers. The one shown in Fig. 72 is a device for generating carbon dioxide under pressure.

The type of extinguisher shown in Fig. 73 is a smaller metal cylinder filled with the liquid known as carbon tetrachloride (CCl_4) and fitted with a sort of piston for forcing the liquid out in case of fire. The liquid is not combustible and is quite volatile; hence when it is thrown onto a fire it volatilizes, and the vapor, being very heavy, surrounds the burning body and prevents the oxygen of the air from coming in contact with it. Other forms of fire extinguishers will be described in connection with the reactions involved in their use (§ 614).

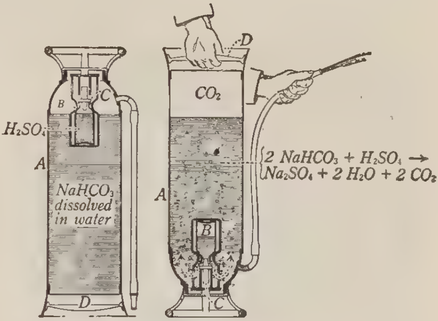

B
C
H₂SO₄
A
NaHCO₃ dissolved in water
D
D
CO₂
2 NaHCO₃ + H₂SO₄ → Na₂SO₄ + 2 H₂O + 2 CO₂
A
B
C

FIG. 72. One form of portable fire extinguisher

The liquid is a solution of sodium bicarbonate ($NaHCO_3$) in water contained in a metal cylinder. The bottle *B* contains sulfuric acid. In case of fire the apparatus is grasped by the handle *D* and inverted as shown in the second figure. The stopper *C*, resting on the top of the bottle *B*, drops down onto the support. The acid flows slowly from the bottle and at once reacts with the sodium bicarbonate, generating carbon dioxide (see equation on the figure). Some of the gas thus generated dissolves in the water, while the remainder forces the water out through the nozzle. While the volume of water so obtained is not large, it is much more effective as a fire extinguisher than a stream of ordinary water because the carbon dioxide present assists in the process

Carbon Monoxide

171. Carbon monoxide (CO). This compound resembles carbon dioxide in being a colorless, odorless gas. It differs from it in being inflammable and very poisonous. It burns with a pale blue flame, forming carbon dioxide:

$$2\,CO + O_2 \longrightarrow 2\,CO_2$$

Because of its strong affinity for oxygen, it is a good reducing agent. If passed over hot copper oxide, for example, metallic copper and carbon dioxide result.

FIG. 73. Extinguishing an automobile fire with carbon tetrachloride

In the laboratory, carbon monoxide is usually prepared by heating formic acid (H_2CO_2) with sulfuric acid:

$$H_2CO_2 \longrightarrow H_2O + CO$$

The sulfuric acid is not included in the equation because it is used only to assist in the reaction by absorbing the water formed.

Carbon monoxide is also formed whenever carbon, in the form of coke or hard coal, is used as a fuel in a furnace or stove, such as pictured in Fig. 74. In such stoves the carbon dioxide at first formed rises through the glowing coals, and is reduced to carbon monoxide (§ 163):

$$CO_2 + C \longrightarrow 2\,CO$$

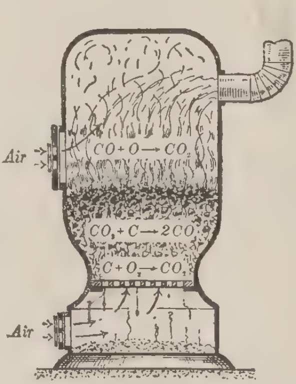

Air
$CO + O \rightarrow CO_2$
$CO_2 + C \rightarrow 2\,CO$
$C + O_2 \rightarrow CO_2$
Air

FIG. 74. Formation of carbon monoxide when hard coal is burned in a stove

If there is plenty of air and not too much cold coal on top, this carbon monoxide burns above the coal with the pale blue flame so characteristic of hard coal fires. If the supply of air is limited, a part of the monoxide passes off as one of the products of combustion.

Carbon monoxide is also formed when gas is burned in stoves and grates and the flame allowed to strike against any cold object such as a kettle of water or even, before it grows hot, the stove or grate itself. Carbon monoxide has a high kindling temperature (§ 50), and the flame is chilled to a point below the kindling temperature of this oxide so that any of it present in the flame escapes unchanged.

172. Precautions against poisoning by carbon monoxide. Carbon monoxide is very poisonous, since it combines with one of the constituents of the red corpuscles of the blood and renders them unfit to carry oxygen to the body cells. *It is also a very treacherous poison because it has no odor and so gives no warning of its presence. Some fuel gases* (§ 469) *contain carbon monoxide. Many deaths result each year from the escape of these gases into the air of rooms and factories, thus rendering the air poisonous. All stoves and grates should have suitable chimney connections to conduct away any carbon monoxide formed in the combustion of the fuel used.*

Another source of poisoning from carbon monoxide is the breathing of the air in a closed garage in which an automobile engine is allowed to run. The exhaust gases of such engines contain from 4 to 12 per cent of carbon monoxide, so that the air in such a garage is soon rendered very dangerous. *Each year many a person loses his life by working in a closed garage in which an engine is running* (Fig. 75).

It is interesting to note that birds are very sensitive to carbon monoxide. In mine explosions carbon monoxide is always formed, and rescuers often carry canaries with them, the death of the birds warning the rescuers of their own peril (Fig. 76).

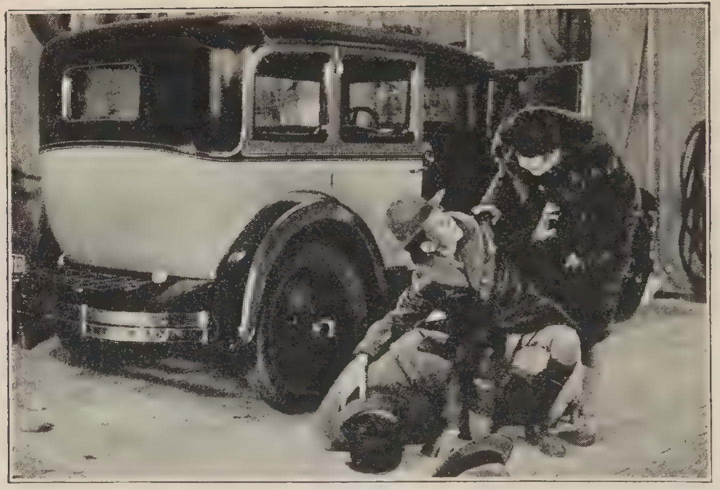


FIG. 75. Carbon-monoxide poisoning in a closed garage

The boy is about to apply first-aid treatment and also is telling his mother to call a physician. (Photograph by the United States Bureau of Mines)

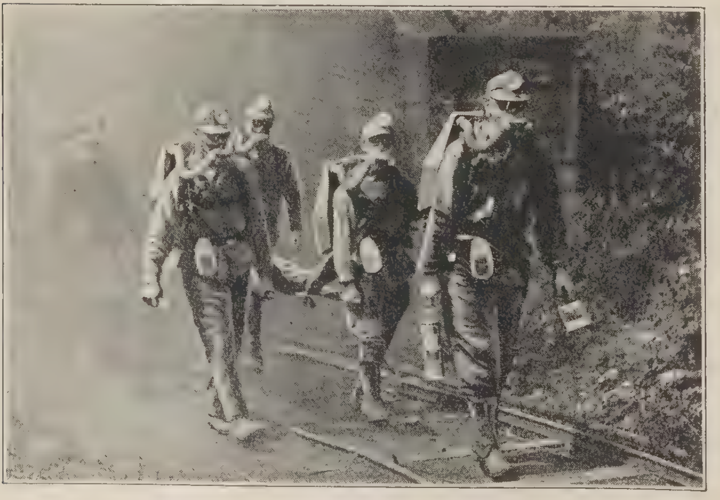


FIG. 76. Mine rescuers provided with gas masks and living canaries

173. Avogadro's law applied to the solution of problems. By applying Avogadro's law we can easily solve a number of problems that have to do with the volume relations of gases. The following will serve to illustrate the kind of problems that can be solved in this way as well as the method to be used.

1. Knowing the formula of a gaseous element or compound, calculate the *approximate* weight of 1 liter of the gas.

Example

The formula of carbon dioxide is CO_2. Calculate the approximate weight of 1 liter of this compound.

Since the formula is CO_2, its molecular weight must be equal to 12 (atomic weight of carbon) $+ 2 \times 16$ (atomic weight of oxygen), or 44. But we have seen that the number which represents the molecular weight of a gaseous element or compound also equals the weight in grams of 22.4 liters of the gas (§ 130). Hence 22.4 liters of carbon dioxide weigh 44 g., and 1 liter weighs $44 \div 22.4$, or 1.9643 g.

The steps involved in solving problems of this type are (1) to calculate the molecular weight of the gas from its formula, and (2) to divide the number representing its molecular weight by 22.4.

The results obtained by this method are only approximate. Thus we obtained the value 1.9643 g. as the weight of 1 liter of carbon dioxide. The real value is 1.9768 (see table facing back cover). The reason why the results are only approximate is that many gases do not act strictly in accordance with the gas laws.

2. Knowing the equation for the reaction that takes place between certain gases, calculate the relative volumes of the gases that enter into the reaction.

Example

Suppose you burn 100 liters of carbon monoxide. (*a*) How many liters of oxygen will be required to burn it, and (*b*) how many liters of carbon dioxide will be formed?

The equation for the reaction (§ 171) is

$$2\ CO + O_2 \longrightarrow 2\ CO_2$$

In other words, 2 molecules of carbon monoxide combine with 1 molecule of oxygen to form 2 molecules of carbon dioxide. Avogadro's law, however, tells us that equal volumes of gases correspond to equal numbers of molecules, so that we may substitute the word "volume" for the word "molecule" in reading the above equation and say that 2 volumes of carbon monoxide combine with 1 volume of oxygen to form 2 volumes of carbon dioxide. It follows, then, that 100 liters of carbon monoxide combine with 50 liters of oxygen to form 100 liters of carbon dioxide. These facts may be represented as follows:

$$\begin{array}{lrcl} & 2\ CO + O_2 & \longrightarrow & 2\ CO_2 \\ & \text{2 molecules} + \text{1 molecule} & \longrightarrow & \text{2 molecules} \\ & \text{2 volumes} + \text{1 volume} & \longrightarrow & \text{2 volumes} \\ \text{or} & \text{100 liters} + \text{50 liters} & \longrightarrow & \text{100 liters} \end{array}$$

The steps involved in solving problems of this type are as follows: (1) write the equation for the reaction involved; (2) note the relation between the numbers of molecules of the gases taking part in the reaction. This relation is the same as the relation between the volumes of the gases.

CHAPTER SUMMARY IN QUESTION FORM

1. Give the name and formula of each of the oxides of carbon.

2. (*a*) Which of the oxides of carbon is formed when carbon burns in air? (*b*) Under what conditions is this oxide changed into the other oxide?

3. Answer the following questions in reference to carbon dioxide:

(*a*) By what other name is it known?

(*b*) Name three natural sources of the gas.

(*c*) Account for the fact that it can be poured from one vessel into another like water.

(*d*) What property of the gas is utilized in making soda water?

(*e*) What happens to the gas (1) when subjected to very great pressure? (2) when released from such pressure suddenly?

(*f*) Name the chemicals used in the preparation of the gas in the laboratory, and write the equation for their reaction with each other.

4. What would be the effect of removing all the carbon dioxide from the atmosphere?

5. Tell what takes place (*a*) when carbon dioxide is passed into water; (*b*) when it is passed into a clear solution of calcium hydroxide (limewater); (*c*) when it is poured over a flame.

6. Write the equation for the reaction that is used as a test for the presence of carbon dioxide.

7. Name three important commercial uses of carbon dioxide.

8. (*a*) Name the chemicals used in each of the two common kinds of hand fire extinguishers, and (*b*) explain how each of these extinguishers operates.

9. Give (*a*) two physical properties that the two oxides of carbon have in common, and (*b*) two ways in which they differ in chemical conduct.

10. Account for the formation of carbon monoxide (*a*) when hard coal is burned in a stove; (*b*) when a gas flame strikes a kettle of cold water.

11. Name (*a*) a property of carbon monoxide that makes the gas useful; (*b*) one that makes it dangerous.

12. What volume will be occupied by the molecular weight of any gas expressed in grams?

13. Calculate from the formula CO_2 the approximate weight of 1 liter of carbon dioxide. Compare with the actual weight given in table facing back cover.

14. Write the equation to represent the reaction that takes place when carbon monoxide burns.

15. Show how by simple inspection of the above equation you can tell the relative volumes of the gases entering into the reaction and formed in it.

THOUGHT QUESTIONS

1. (*a*) How is the low temperature necessary to solidify carbon dioxide obtained? (*b*) Explain.

2. Why not save money by using air in place of carbon dioxide in making soda water?

3. (*a*) Name the gases that we have so far studied. (*b*) Tell how you could distinguish each one of them.

4. Complete the following table:

	CARBON DIOXIDE	CARBON MONOXIDE
(*a*) Color		
(*b*) Odor		
(*c*) Weight of 1 liter		
(*d*) Occurrence		
(*e*) Relation to combustion . .		
(*f*) Effect when breathed . . .		
(*g*) Uses		

5. Both hydrogen and carbon monoxide burn with an almost colorless flame. How could you tell the difference between the two gases?

6. Suppose you had a mixture of the two oxides of carbon. Suggest a way for determining the relative amounts of the two present.

7. The flame of a lighted candle is sometimes extinguished when the candle is lowered into deep wells. Explain.

8. Name two uses of the carbon dioxide generated in the ordinary hand fire extinguisher.

9. Name possible sources of danger of being poisoned by carbon monoxide.

10. Suppose you added sufficient hydrochloric acid to dissolve 50 g. of marble. (*a*) What weight of carbon dioxide would be evolved? (*b*) What volume?

11. A certain volume of pure carbon monoxide was burned. The carbon dioxide formed had a volume of 60 liters. (*a*) Write the equation for the reaction. Determine by reference to the equation (*b*) the volume of the carbon monoxide burned; also (*c*) the

volume of the oxygen used in the combustion. (In all such problems it is understood that the comparisons of volumes are made under the same conditions of temperature and pressure.)

FOR HONOR STUDENTS

1. Visit your fire department and find out all you can about the fire apparatus called "chemical," such as (*a*) the materials in charging and the weight of each used; (*b*) how the apparatus is recharged after a fire; (*c*) the cost of the materials used in charging; (*d*) chemical reactions when in operation.

2. Suppose that the water in the fire extinguisher shown in Fig. 72 contained 4 kg. of sodium bicarbonate in solution. (*a*) What weight of hydrogen sulfate must the sulfuric acid in bottle *B* contain so that all the carbon dioxide may be evolved from the bicarbonate? (*b*) What weight of carbon dioxide would be evolved when the fire extinguisher is used? (*c*) What volume would this weight of the gas have?

3. On a general average, a person exhales about 8 liters of air per minute, containing approximately 4 per cent by volume of carbon dioxide. Suppose there were 100 students in a schoolroom, and that there was no ventilation. How many liters of carbon dioxide would be added to the air of the room each hour?

CHAPTER XIII

VALENCE

How Atoms fit Together

174. *Introduction.* In Chapter X we learned about the ratio in which atoms combine *by weight* and the way these relative weights are used in formulas and equations. A glance at the formulas we have been using will show that in addition to combining in definite ratios *by weight,* the atoms fit together in molecules in definite ratios *by number*. These *number ratios* depend upon a property of each kind of atom called its *valence,* and a study of this property will be of great help in writing equations.

175. Valence of atoms. We can get a clear idea of what is meant by the valence of an atom by noting the formulas of the compounds in the equation (§ 165):

$$CaCO_3 + 2\,HCl \longrightarrow CaCl_2 + H_2O + \overline{CO_2}$$

It will be seen that 1 atom of hydrogen combines with 1 atom of chlorine (HCl), while 1 atom of calcium combines with 2 atoms of chlorine ($CaCl_2$); also that while 1 atom of chlorine combines with 1 atom of hydrogen (HCl), 1 atom of oxygen combines with 2 atoms of hydrogen (H_2O). Later on we shall find that 1 atom of nitrogen combines with 3 atoms of hydrogen (NH_3), while 1 atom of carbon combines with 4 atoms of hydrogen (CH_4). So we have the compounds

$$HCl,\ H_2O,\ H_3N,\ H_4C$$

As another example of this number ratio we have seen that when sodium acts on water, 1 atom of sodium displaces 1 atom of hydrogen, but when zinc acts on sulfuric acid, 1 atom of zinc replaces 2 atoms of hydrogen (§ 152).

The valence of an atom is that property of an atom which determines what number of atoms of another kind it can hold in combination or displace in a reaction, as measured by some standard atom. Valence means *value in numbers,* not in *weight* or *affinity.*

176. Standard of valence. An inspection of all the formulas of compounds containing hydrogen shows that the hydrogen atom never combines with more than *one* atom of any other kind to form a molecule which contains only two kinds of atoms; and in nearly all cases the same is true of the chlorine atom. For this reason the atoms of hydrogen or of chlorine are called *univalent* atoms, and serve as a standard of comparison for the valence of other atoms. Oxygen, sulfur, zinc, and iron, whose atoms combine with two of hydrogen or of chlorine, are called *bivalent* atoms. There are other elements whose atoms have still higher valences, of three (*trivalent*), four (*quadrivalent*), and so on up to a valence of eight. *The atom of hydrogen* (*or of chlorine*) *is thus taken as a standard for valence.*

177. A possible misunderstanding. From all that has been said it might be supposed that in the compound CuO the atoms of both copper and oxygen are univalent, because there is one of each in the molecule. But *measured by hydrogen,* which is our standard, oxygen is bivalent (H_2O); accordingly copper must be bivalent also, as is confirmed by the formula for its chloride, $CuCl_2$. We must always keep in mind that oxygen is *bivalent* when we deduce the valence of an atom from the formula of its oxide.

178. Illustration of valence. The relations of valence may be illustrated by the way in which various sizes of tile fit together in a tile floor (Fig. 77). The small squares (1) correspond to the univalent atoms like hydrogen. It takes two of these to fit beside a rectangular tile (2), which is like oxygen in H_2O. Two rectangular tiles (2) fit together, though each is bivalent, like CuO, while four univalent squares fit the large square (4), like CH_4. Two rectangles (2) fit the large square (4), like CO_2. It will be seen that the space 3 is equivalent to three unit squares and is therefore trivalent, like NH_3.

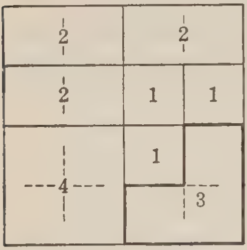


FIG. 77. Illustration of valence

Of course this illustration does not mean that valence depends on the *size* of the atoms, but is intended merely to show how we select a standard valence 1, and infer the valence of other atoms from this standard.

179. Applications of valence. While it is not possible at this point to go very far into the subject of valence, the following general principles will be of service:

1. If two atoms *which have the same valence* combine to form a compound, they will combine atom for atom, as shown in the following formulas, in which the valence of the atom of each element is designated by the figure placed above the symbol:

$$\overset{1}{H}\overset{1}{Cl},\ \overset{2}{Hg}\overset{2}{O},\ \overset{3}{Al}\overset{3}{N},\ \overset{4}{Si}\overset{4}{C}$$

2. If two atoms of different valences combine to form a compound, then such numbers of the two kinds of atoms will combine as will add up an equal number of valence units, thus:

$$\overset{1}{H}_2\overset{2}{O},\ \overset{3}{N}\overset{1}{H}_3,\ \overset{4}{C}\overset{1}{H}_4,\ \overset{4}{C}\overset{2}{O}_2,\ \overset{3}{Al}_2\overset{2}{O}_3$$

In the water molecule, H_2O, there is 1 atom of oxygen (2 valences); so there must be enough hydrogen atoms in each molecule to add up 2 valences, namely, 2 atoms.

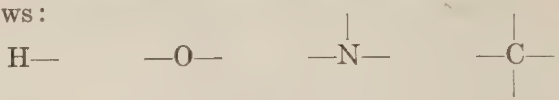
Again, in the formula CO_2 the carbon is quadrivalent (as shown in the formula CH_4). Accordingly, for each atom of carbon (4 valences) there must be 2 atoms of oxygen (4 valences).

3. In any reaction in which one element takes the place of another in a compound, or in which one element of a compound exchanges places with an element in another compound, the exchange must be between such numbers of atoms as will add up an equal number of valence units. For example, one bivalent atom will displace two univalent atoms, while two trivalent atoms (6 valences) will displace three bivalent atoms (6 valences).

$$\begin{gathered}
2\,\overset{1}{\mathrm{Na}} + \overset{1}{\mathrm{H}}_2\mathrm{SO}_4 \longrightarrow \mathrm{Na}_2\mathrm{SO}_4 + \mathrm{H}_2 \\
\overset{2}{\mathrm{Zn}} + 2\,\overset{1}{\mathrm{H}}\mathrm{Cl} \longrightarrow \mathrm{ZnCl}_2 + \mathrm{H}_2 \\
\overset{1}{\mathrm{Na}}\mathrm{OH} + \overset{1}{\mathrm{H}}\mathrm{Cl} \longrightarrow \mathrm{NaCl} + \mathrm{HOH}\ (\text{or } \mathrm{H}_2\mathrm{O}) \\
\overset{2}{\mathrm{Ba}}\mathrm{O}_2 + \overset{1}{\mathrm{H}}_2\mathrm{SO}_4 \longrightarrow \mathrm{BaSO}_4 + \mathrm{H}_2\mathrm{O}_2
\end{gathered}$$

180. Variable valence. As a rule the atoms of any given element do not have one fixed valence. The atoms of most elements have two different valences, and some have more. Thus mercury forms two compounds, $HgCl$ and $HgCl_2$, in which the mercury atom is univalent in the one and bivalent in the other. Similarly, tin and chlorine form compounds with the formulas $SnCl_2$ and $SnCl_4$. A given atom often has one valence for one kind of atom and a different valence for another. Thus sulfur is bivalent in the compound H_2S but quadrivalent in the compound SO_2.

181. Method of representing valence. It is often convenient to represent the valences of elements in a graphic way, and this is commonly done by lines drawn from the symbols of the elements, one line (or *bond*, as it is often called) expressing a single valence. In this way we may represent the valence of hydrogen (univalent), oxygen (bivalent), nitrogen (trivalent), and carbon (quadrivalent) as follows:



$$\mathrm{H}- \qquad -\mathrm{O}- \qquad -\overset{|}{\mathrm{N}}- \qquad -\underset{|}{\overset{|}{\mathrm{C}}}-$$

When hydrogen unites with oxygen to form water (H_2O), we have every reason for believing that each of the two atoms of hydrogen is combined directly with oxygen, and this fact can be expressed by the formula H— —O— —H or, more simply, H—O—H, in which the two valences of the hydrogen atoms *saturate* the two valences of the oxygen atom. Such a formula is known as a *structural formula.*

182. Puzzling cases of valence. In applying the rules of valence, the student will meet with many cases which (at first sight at least) are misleading. For example, in the formula for hydrogen peroxide, H_2O_2, one would be inclined to say that oxygen and hydrogen have the same valence; and the formula for iron oxide, Fe_3O_4, would indicate that the iron atom has a valence of $2\frac{2}{3}$, which evidently cannot be the fact. Puzzling cases of this kind will become clear in later chapters.

183. Table of valences. The usual valences of the elements will become familiar as we go along and meet with the formulas of their compounds. In the following table, however, are given the usual valences of the most important elements:

VALENCE OF ELEMENTS

I. Univalent	H, Na, K, Ag, Cl, Br, I
II. Bivalent	Ca, Ba, Mg, Zn, Hg, Fe, S, O
III. Trivalent	Al, Bi, As, Sb, Fe, N, P
IV. Quadrivalent	Sn, C, Si, S
V. Quinquivalent	N, P, As, Sb

184. Explanation of valence. It will be noticed that so far we have dealt with valence merely as an *experimental fact,* and have made no attempt to show *why* the atoms of different elements have different valences. Evidently so striking a fact should lead chemists to try to imagine a plausible theory to account for the fact of valence, and the student will want to know something about such a theory. A little reflection will convince the student that since valence is a peculiar property of the *atom*, the real explanation of valence must be looked for in the *structure of the atom*. The next chapter will be devoted to this subject, and will suggest a theory to account for valence.

CHAPTER SUMMARY IN QUESTION FORM

1. Show by formulas of compounds that one atom of each of the elements chlorine, oxygen, nitrogen, and carbon combines with a different number of hydrogen atoms.

2. By reference to question 1 explain what is meant by the word *valence*.

3. What is the standard used in determining the valence of an element?

4. How is the valence of an element found?

5. Give the names of the classes into which elements are divided in accordance with their valence.

6. In what ratio will (*a*) atoms of the same valence combine? (*b*) atoms of different valence?

7. When one element takes the place of another in a reaction, the exchange is between what numbers of the two atoms?

8. Does the same element always have the same valence?

9. How do we sometimes represent the valence of an element?

10. Illustrate the difference between molecular formulas and structural formulas by writing each of these formulas for water.

THOUGHT QUESTIONS

1. Determine the valence of sodium from the following equation: $2\ Na + 2\ HCl \longrightarrow 2\ NaCl + H_2$.

2. Copper forms the two oxides CuO and Cu_2O. What is the valence of copper in each of these oxides?

3. (*a*) Recall the formulas of the two oxides of carbon. (*b*) What is the valence of carbon in each of these compounds?

4. Zinc is bivalent and chlorine univalent in zinc chloride. Give the formula for this compound.

5. Aluminum is trivalent, and oxygen bivalent. Write the formula for aluminum oxide.

6. State the valence of iron in the following compounds: $FeCl_2$; Fe_2O_3; FeO.

7. Sulfur forms two oxides, in one of which the sulfur is quadrivalent and in the other hexavalent. Write the formulas for each of these oxides.

8. Bismuth forms the oxide Bi_2O_3. Write the formula that you would expect bismuth chloride to have.

9. Complete and balance the following equation, in which the hydrogen and bismuth exchange places: $H_2S + BiCl_3 \longrightarrow$

10. Gold is trivalent. Write the formula for gold chloride.

FOR HONOR STUDENTS

1. Copy Fig. 78 (or a similar one) on a piece of white cardboard; then cut it into sections along the heavy lines. The numerals represent valence. Thus *A* represents one atom of a univalent element; *B*, one atom of a bivalent element; *E*, one atom of a quinquivalent element.

By placing one or more strips of one kind under one or more of another, represent the compound formed by the following combinations: *A* and *B*; *A* and *C*; *B* and *C*; *B* and *D*; *B* and *E*.

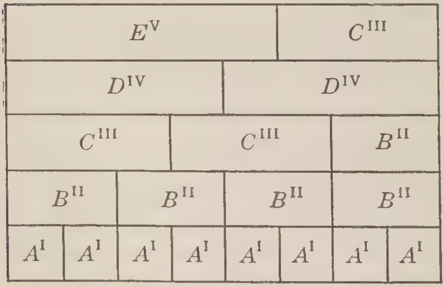


FIG. 78. Exercise in valence

2. Select the various compounds so far used or studied that contain but two elements, and show which of the above combinations each represents.

CHAPTER XIV

THE STRUCTURE OF THE ATOM

Each Atom a Little Solar System

185. *Introduction.* How can we account for the *facts* of valence? Why does one atom of oxygen combine with two atoms of hydrogen and with but one atom of zinc? What is the *explanation* of this number ratio?

Until a few years ago no satisfactory answer could be given to these questions. Now the physicist has demonstrated that electricity as well as matter is atomic in its make-up, and it is becoming possible to explain valence as due to the electrical nature of matter. It will not be possible to explain how the facts about to be stated have been found out, since this would require a great deal of mathematics, but the facts are based on the results of a great many experiments.

186. Two kinds of electricity. For more than a century electricity has been regarded as being of two kinds, which, for want of better names, have been called *positive* electricity and *negative* electricity. It has also been a matter of common knowledge that a body charged negatively and another charged positively attract each other.

A great advance has been made in our knowledge of electricity during recent years, so that now electricity and matter are regarded as forms of the same thing. Moreover, we know that electricity consists of two kinds of electrical units or charges or electrical "atoms," each having a definite weight, like the atoms of ordinary elements. The "atom" of what we have been calling positive electricity is named the *proton,* and in weight is just a trifle lighter than the hydrogen atom. The "atom" of negative electricity is named the *electron*, and this is only about $\frac{1}{1845}$ as heavy as the hydrogen atom. While these two kinds of "atoms" differ so greatly in weight, nevertheless their electrical charges, while opposite in character, are equal; so that a body made up of the *same number* of protons and electrons, whatever that number may be, will be electrically neutral.

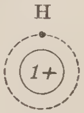
187. Electrical composition of ordinary atoms. One of the most surprising achievements of science has been to show that *the atoms of any given element are made up of protons and electrons in equal numbers.* The weight of any given atom is simply the sum of the weights of the protons and electrons of which it is composed; and since the weight of the electron is so very small, the weight of the atom is practically equal to the weight of its protons. Thus the hydrogen atom (atomic weight = 1) consists of 1 proton and 1 electron; the atom of helium (atomic weight = 4), of 4 protons and 4 electrons; the atom of oxygen (atomic weight = 16), of 16 protons and 16 electrons.

188. Electrical neutrality. It is a well-known fact that equal quantities of positive and of negative electricity neutralize each other. In terms of our present theory we say that when equal numbers of protons and electrons combine, the properties we have called *electrical* disappear, and the product has the characteristics of neither the proton nor the electron, just as water has the properties of neither hydrogen nor oxygen.

189. Arrangement of protons and electrons in the atom. The protons and electrons are not thrown together in a jumble to make an atom, but each kind of atom, such as hydrogen or helium or oxygen, has its own wonderful organization consisting of two parts: a *nucleus*, or central body, and one or more electrons apart from the nucleus, called *satellite electrons*.

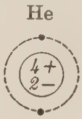
190. The nucleus. All the protons and *about* half the electrons are concentrated in the very dense central nucleus. The electrons in the nucleus are sometimes called *nuclear* electrons or *binding* electrons. Since the nucleus consists of more protons than binding electrons, it is always strongly *positive.*

191. The satellite electrons. The remaining electrons of the atom (*about* half), all of which are, of course, *negative,* revolve around the central nucleus, or are spaced about it in definite orbits or positions, much as the various planets revolve around the central sun.



A.N. 1

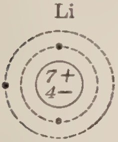
FIG. 79



A.N. 2

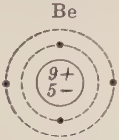
FIG. 80

192. General arrangement of nucleus and of satellite electrons. The results of many experiments have shown that we may represent the structure of the ten lightest atoms, in the order of their atomic weights, by Figs. 79 to 88. A proton is indicated by the plus sign (+) and an electron by the minus sign (−) or by a dot on an orbit. The nucleus is the central circle, and the satellite electrons are in the orbits drawn around the nucleus.



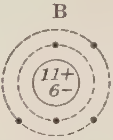
A.N. 3

FIG. 81



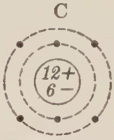
A.N. 4

FIG. 82



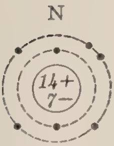
A.N. 5

FIG. 83



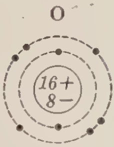
A.N. 6

FIG. 84



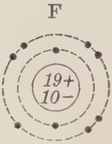
A.N. 7

FIG. 85



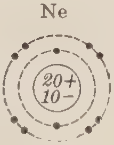
A.N. 8

FIG. 86



A.N. 9

FIG. 87



A.N. 10

FIG. 88

193. The charge of the nucleus. The hydrogen atom is made up of 1 proton and 1 satellite electron (Fig. 79), and so the nucleus consists of but a single proton (+). In all other atoms the nucleus is made up of both protons (+) and a smaller number of binding electrons (−), and so (as with the hydrogen atom) the charge of the nucleus is always positive. By the term *positive charge* we mean the number of protons (+) minus the number of binding electrons (−). In the helium atom (Fig. 80) the nuclear charge is 2, in the lithium atom (Fig. 81) it is 3, in the beryllium atom (Fig. 82) it is 4, and so on. The nuclear charge increases by a unit with each successive atom. The nuclear charge of neon (Fig. 88) is 10. *The number of positive units constituting this charge of the nucleus is called the atomic number of the atom.* The letters A.N. below each figure indicate the (positive) charge of the nucleus or the *atomic number* of the element.

Since the weight of an atom depends almost wholly upon its protons, a list of the elements arranged according to atomic numbers is almost the same as the list arranged according to atomic weight.

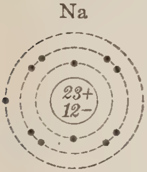
194. The arrangement of the satellite electrons. Since equal numbers of protons and electrons constitute an atom, it follows that for every positive charge of the nucleus there must be one electron as a satellite *outside* of the nucleus; so the atomic number gives not only the positive charge of the nucleus but also *the total number of satellite electrons.*

The hydrogen atom has one satellite electron; the helium atom two, both in the same orbit relatively near the nucleus. The next atom, lithium, has three satellite electrons. Two of these, like the satellites of helium, are in an orbit close to the nucleus; the third is in a more distant orbit. As the number of satellites increases, they take their places in this outer orbit until we reach neon, with its two inner satellites and eight more distant ones. The table at the top of the next page sums up these relations.

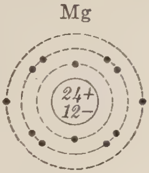
THE ATOM IN TERMS OF PROTONS AND ELECTRONS

Symbol	H	He	Li	Be	B	C	N	O	F	Ne
Atomic number	1	2	3	4	5	6	7	8	9	10
Nuclear charge	1	2	3	4	5	6	7	8	9	10
Satellite electrons	1	2	3	4	5	6	7	8	9	10
Nuclear protons	1	4	7	9	11	12	14	16	19	20
Nuclear electrons	0	2	4	5	6	6	7	8	10	10
Atomic weight	1	4	7	9	11	12	14	16	19	20

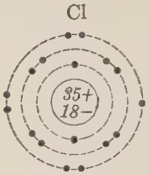
195. Atoms with more than ten satellite electrons. In the sodium atom, of atomic number 11, the eleventh satellite electron is in an orbit still more distant from the nucleus than is the orbit of the eight outer electrons of neon, as represented in Fig. 89. The magnesium atom has two of these more distant electrons (Fig. 90). With successively higher atomic numbers, more and more electrons take their places in this new outer orbit, until we reach chlorine (atomic number 17) and argon (atomic number 18), which are represented in Figs. 91 and 92. The *fourth* orbit is not filled until it contains eighteen electrons, but we shall not consider atoms beyond argon.



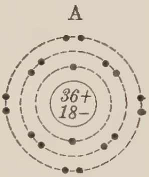
A.N. 11
FIG. 89



A.N. 12
FIG. 90



A.N. 17
FIG. 91



A.N. 18
FIG. 92

196. To find the structure of an atom. From the description given in the preceding pages it is not difficult to arrive at the structure of any of the first twenty or more atoms. As an example, let us work out the structure of the sulfur atom.

Its atomic weight, 32, at once tells us that it is made up of 32 protons and 32 electrons. Its atomic number is 16 (see table on inside back cover page), and so the positive (+) charge of the nucleus is 16. In addition to 32 protons, the nucleus therefore contains 32 – 16, or 16, electrons. The other 16 electrons are satellites. Of these, 2 will be in the innermost orbit and 8 in the second, which leaves 6 in the third orbit.

197. Completed orbits. From this sketch we see that the first orbit is completely full when it contains two electrons, while the second and third orbits are completed by eight electrons each. These facts have an important bearing on valence.

198. Atoms of no valence. Experiment has shown that those atoms which have *completed outer orbits* do not combine with any other atoms. In other words, they have no chemical affinity for anything and consequently no valence. The helium atom has the first orbit completed with two electrons; the neon atom has the second orbit completed with eight electrons; the argon atom has the third orbit completed with eight electrons. No one of these atoms forms any chemical compound.

199. Chemical action tends to complete outer orbits. The facts just described suggest the idea that chemical action takes place in such a way as to complete the outer orbits of as many atoms as possible. This might occur in either of two ways:

1. *By loss or gain of electrons — polar compounds.* An atom may surrender one or more of its electrons from an incomplete outer orbit, or it may capture electrons from some source to fill up its outer orbit to the complete number.

Thus the lithium atom (Fig. 81), with only one electron in its outer orbit, may hand over this lone satellite to some other atom whose outer orbit is nearly complete — say to the fluorine atom (Fig. 87), which needs but one more. Both atoms will then have completed outer orbits — the lithium atom with two electrons, the fluorine atom with eight electrons. We may represent this reaction by Fig. 93. The lithium atom, having *lost* one electron, now has merely its completed inner orbit, but is *positive* (+) by one unit charge since it consists of one more proton than electron. The fluorine atom has *gained* one electron, thus completing its outer orbit of eight electrons, and is now *negative* (−) in charge. The two modified atoms, one positive and the other negative, are held together by the attraction of these opposite charges.

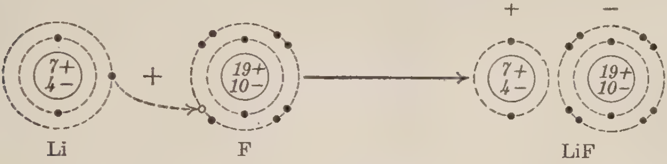


FIG. 93. The reaction: $Li + F \longrightarrow LiF$

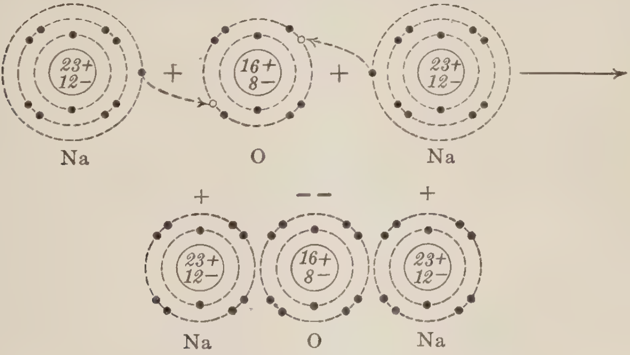


FIG. 94. The reaction: $2\,Na + O \longrightarrow Na_2O$

The sodium atom, like the lithium atom, has one lone electron in its outer orbit (Fig. 89), while the oxygen atom (Fig. 86) has six and so needs two to complete this orbit. We may represent the action of sodium on oxygen by Fig. 94. Each of the two atoms of sodium has *surrendered* the lone electron in its outer orbit, and has now a completed outer orbit of eight electrons; each is *positive* by one charge. The oxygen atom has *acquired* two electrons, and has filled up the vacant places in its outer orbit of eight electrons; it is *negative* by two charges. The three atoms are held together in a molecule by these opposite charges. *Compounds formed by interchange of electrons are called polar compounds.*

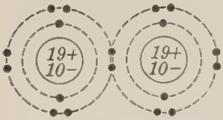


FIG. 95. The fluorine molecule (F_2)

2. ***By sharing pairs of electrons — nonpolar compounds.*** Instead of actually gaining or losing electrons, *two atoms may share electrons.* When this happens, the two atoms always share one or more *pairs* of electrons — never single ones. When pairs of electrons are shared, the outer orbits of the two atoms have one or more pairs of electrons *in common.* Thus, two atoms of fluorine share one pair of electrons in forming a molecule of fluorine, F_2 (Fig. 95). Two atoms of oxygen share two pairs of electrons in forming a molecule of oxygen, O_2 (Fig. 96). In both cases the outer orbit of each of the atoms is a completed one. *Compounds formed by sharing pairs of electrons are called nonpolar compounds.* In general it may be said that more molecules are held together by sharing electrons (nonpolar compounds) than by interchange of electrons (polar compounds).

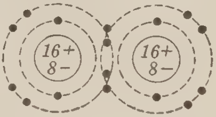


FIG. 96. The oxygen molecule (O_2)

200. Lending and borrowing atoms. We may, then, look upon some atoms as either *lenders* or *borrowers* of electrons while other atoms tend to share electrons. Atoms with only one, two, or even three electrons in their outer orbits (like hydrogen, lithium, sodium, beryllium) tend to *lose* electrons, and are *lenders.* Atoms which lack one, two, or even three electrons in their outer orbits (like fluorine, chlorine, oxygen) tend to *capture* electrons, and are *borrowers.*

201. Atomic structure and valence. We can now see a very good *reason* for valence. *The valence of an atom is due to loss or gain of electrons* or to sharing them in pairs. The atom that loses or gains one electron during chemical change or shares a pair with another atom is a *univalent* atom; while one which loses or gains two electrons or shares two pairs is a bivalent atom. It is also clear why valence is a *number* ratio and is always expressed by a whole number (integer). An atom cannot lose or gain a fraction of an electron, for electrons are indivisible.

202. Positive and negative valence. It is often desirable to specify whether the valence of an atom is due to the *loss* or to the *gain* of an electron. So we say that an atom which tends to lose electrons (and so becomes positive) has positive valence of 1, 2, or 3; while an atom that tends to borrow electrons (and so becomes negative) has negative valence of 1, 2, or 3.

203. Valence electrons. It will be noticed that it is only the electrons *in the outer incomplete orbits* that are concerned with the chemical conduct of an atom and that give the atom its valence. Consequently the electrons in the outer incomplete orbits are called the *valence electrons* of the atom.

204. Variable valence. We can also see why the valence of an atom may be *variable.* An atom with two or three valence electrons may lend sometimes one of these, sometimes two or even all three, depending upon the urgency of the need of the borrowing atom; atoms that lack one, two, or three electrons may at times succeed in borrowing *all* they need, and under other conditions only a part.

205. Fractional atomic weights. It will not escape the notice of the thoughtful student that, since the weight of the proton is 1 while that of the electron is practically negligible, *the atomic weights of all the elements should be* *exact multiples of 1*; that is, they should all be whole numbers. An inspection of the table of atomic weights (inside back cover page) shows that this is not at all true, for many atoms have fractional atomic weights. The reason for this lack of agreement will be given in a later chapter.

206. The composition of matter. In speaking about the composition of matter in previous chapters, we have said that matter is composed of molecules. We have also said that matter is composed of atoms, and in the present chapter we are saying that matter is composed of protons and electrons. These statements may seem confusing, but we can readily understand that they are all true when expressed in the following way: *all matter is composed of molecules; these in turn are composed of atoms, and the atoms in turn are made up of protons and electrons.* We may well ask whether protons and electrons are really the ultimate units of matter. We have thought so, but physicists and chemists agree that much still remains to be found out about the real nature of these wonderful electrical units.

207. A word about theories. In this picture of the structure of the atom we have another typical scientific theory. The experimental *facts* cannot well be doubted, but many details of the picture are unsatisfactory and will undoubtedly be modified from year to year. In its present form the theory corresponds very well with many known facts, and in addition gives us a vivid picture of valence. We can with advantage use this picture theory if we keep in mind that it is largely a *theory*.

CHAPTER SUMMARY IN QUESTION FORM

1. In what way does electricity resemble matter?

2. (*a*) Name the two kinds of electrical units. (*b*) Compare them in weight and in electrical charge.

3. Of what are the atoms of the elements composed?

4. Are the atoms (*a*) positively charged? (*b*) negatively charged? (*c*) electrically neutral?

5. Give in general the arrangement of the protons and electrons in an atom of any element.

6. Of what is the nucleus composed?

7. (*a*) Where are the protons in any atom located? (*b*) Where are the electrons?

8. What name do we give to those electrons that revolve around the nucleus?

9. How do the number of electrons in the nucleus compare with the number outside the nucleus?

10. Draw diagrams from memory showing the structure of the atoms of four different elements.

11. What sign is used to represent (*a*) a single positive charge? (*b*) a single negative charge?

12. What name is given to the number of positive units constituting the charge on the nucleus equal in number to the satellite electrons?

13. A given atom has a nucleus composed of 16 protons and 8 electrons. (*a*) How many satellite electrons are there in the atom? (*b*) What is the charge of the nucleus? (*c*) What is the atomic number of the atom?

14. Draw a diagram showing the position of the satellite electrons in (*a*) an atom of atomic number 1; (*b*) an atom of atomic number 2; (*c*) an atom of atomic number 6.

15. How many electrons constitute (*a*) the first complete orbit? (*b*) the second? (*c*) the third?

16. Name (*a*) three elements whose atoms have completed outer orbits; (*b*) three that have incompleted outer orbits.

17. What are the electrons in the incomplete orbits called?

18. From the standpoint of atomic structure, of what does chemical action consist?

19. In what two ways may an atom complete an outer orbit?

20. How do our modern views concerning the structure of the atom account for valence?

THOUGHT QUESTIONS

1. Account for the fact that an atom is electrically neutral.

2. How does the atomic weight of any element compare (*a*) with the weight of the electrons in an atom of the element? (*b*) with the weight of the protons in the atom?

3. The atomic weight of carbon is 12; its atomic number is 6. Draw a diagram of the carbon atom.

4. How can you tell from the number of electrons in the outer orbit of its atom whether any given element is chemically active or inert?

5. Give the structure in the outer orbit of an atom of (*a*) a univalent element; (*b*) a bivalent element; (*c*) a trivalent element.

6. Distinguish between positively charged substances and negatively charged substances in terms of electrons.

7. (*a*) How does the electron theory account for variable valence? (*b*) How does it account for the fact that an element such as argon does not combine with any other element?

8. Tell which of the following statements is correct: (*a*) matter is composed of molecules; (*b*) matter is composed of atoms; (*c*) matter is composed of protons and electrons.

FOR HONOR STUDENTS

Using a large wooden bead for the nucleus, small beads for each of the satellite electrons, and wire for the orbits of the electrons, construct models of the atoms of one or more different elements. (These beads can be purchased at any ten-cent store.)

CHAPTER XV

CHLORINE; HYDROGEN CHLORIDE; HYDROCHLORIC ACID

208. *Introduction.* At the same time that Priestley (Fig. 14) was carrying on in England his famous experiments which led to the discovery of oxygen and a number of other gases (§ 37), the great chemist Scheele (Fig. 97) was making equally important experiments in Sweden. While still a young man Scheele was apprenticed to a pharmacist and in this way became familiar with various chemical substances. He soon began experimenting with these, and in his lifetime made many important discoveries. Indeed, it seems probable that Scheele prepared oxygen before Priestley, but he did not publish his results at the time. In the same year (1774) in which Priestley is credited with the discovery of oxygen, Scheele obtained a greenish yellow gas to which the name *chlorine*

FIG. 97. Karl Wilhelm Scheele (1742–1786)

This Swedish chemist was one of the greatest experimenters of his century. He discovered oxygen independently of Priestley, as well as the elements chlorine, tungsten, and molybdenum. He prepared the deadly gases arsine and prussic acid. He first isolated many organic compounds, such as glycerin and oxalic, tartaric, and citric acids. Scheele was one of the ablest as well as one of the latest defenders of the phlogiston theory of combustion was later given, the name being derived from a Greek word signifying "greenish yellow."

The gas so discovered was used almost a hundred and fifty years later in chemical warfare. Almost all the poison gases used in the World War were either free chlorine or some compound of chlorine (Fig. 100). This fact warns us to be careful, while working with chlorine, *not to breathe the gas*. When inhaled even in minute quantities it acts injuriously upon the throat and lungs, and larger quantities may easily prove fatal.

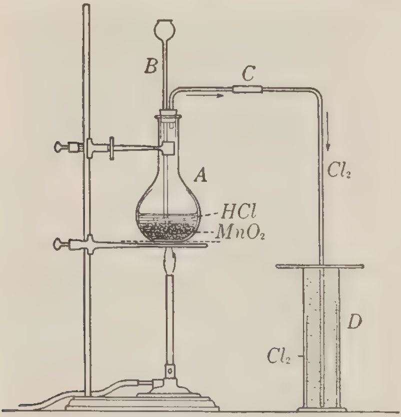


FIG. 98. The preparation of chlorine

Manganese dioxide is placed in the flask *A* and hydrochloric acid is added through the funnel tube *B*. Chlorine gas escapes through the tube *C*. Since it is much heavier than air, it is delivered at the bottom of the bottle *D*, and fills the bottle by displacing the air upward

209. Occurrence. Unless we have studied chemistry we are not likely to know much about chlorine, for the element is not found free in nature, although its compounds are present in our bodies, in our foods, in the soil, and in all natural waters. Its most abundant compounds are those in which the chlorine is combined with a metal, forming a *chloride*. Thus all salt waters contain in solution sodium chloride (NaCl), potassium chloride (KCl), and magnesium chloride ($MgCl_2$). Of these, sodium chloride, or *common* salt as we usually call it, is far the most abundant, and for that reason is the one used in preparing chlorine as well as the compounds of chlorine.

210. Preparation. Scheele first obtained chlorine by the action of hydrochloric acid on manganese dioxide, the black compound we used in preparing oxygen (§ 40), and this method is still the most common one used for preparing the gas in the laboratory. When these two compounds are heated together (Fig. 98), manganese tetrachloride ($MnCl_4$) is formed at first, but it is unstable and breaks down into manganous chloride ($MnCl_2$) and chlorine (Cl_2), thus:

$$MnO_2 + 4\,HCl \longrightarrow MnCl_4 + 2\,H_2O$$
$$MnCl_4 \longrightarrow MnCl_2 + Cl_2$$

Instead of the hydrochloric acid in this reaction it serves just as well to use a mixture of sodium chloride and sulfuric acid, since these two compounds react to form hydrochloric acid. In this case the complete reaction is expressed by the following equation:

$$MnO_2 + 2\,NaCl + 2\,H_2SO_4 \longrightarrow Na_2SO_4 + MnSO_4 + 2\,H_2O + Cl_2$$

211. The commercial method for preparing chlorine. While the method just described for preparing chlorine is easy to carry out, and well adapted to the laboratory where only small quantities are desired, it is rather expensive. When wanted in large quantities, chlorine is always prepared by the electrolysis of a solution of sodium chloride. Under these conditions chlorine is evolved at the anode and sodium is set free at the cathode (Fig. 55). The sodium, however, at once reacts with the water present, forming sodium hydroxide and hydrogen:

$$2\,Na + 2\,H_2O \longrightarrow 2\,NaOH + H_2$$

The hydrogen is evolved, while the sodium hydroxide (being a soluble solid) remains dissolved in the water about the cathode.

While Fig. 55 represents the principles involved in the electrolysis of sodium chloride, the actual apparatus used is rather complicated because it is necessary to prevent the chlorine from coming into contact with the sodium hydroxide formed, for these two substances react. Many different forms of electrolytic apparatus have been devised for preparing chlorine, each one known as a cell. One of the common forms, called the Vorce cell from its inventor, is shown in cross section in Fig. 99 (see also Fig. 101).

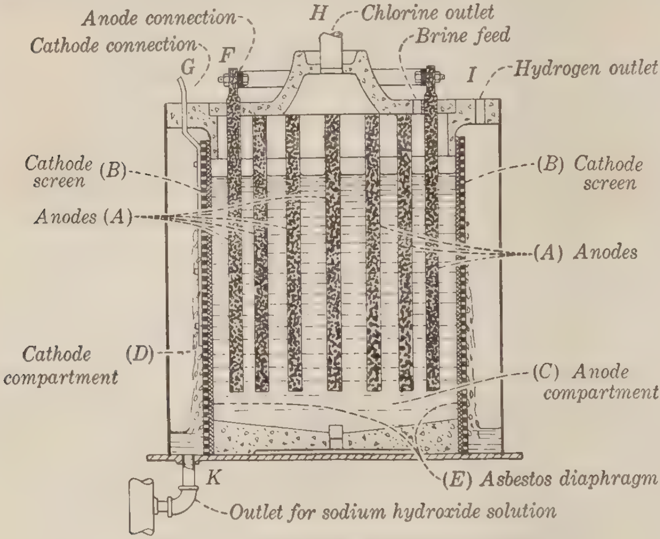

Anode connection
Cathode connection
G
F
H
Chlorine outlet
Brine feed
I
Hydrogen outlet
Cathode screen (B)
(B) Cathode screen
Anodes (A)
(A) Anodes
Cathode compartment
(D)
(C) Anode compartment
K
(E) Asbestos diaphragm
Outlet for sodium hydroxide solution

FIG. 99. The Vorce cell for producing chlorine

The salt brine is placed in a large cylindrical container and renewed from time to time through the brine feed. A number of graphite anodes A are dipped into the brine. The cathode of wire screening B surrounds the group of anodes in the form of a hollow cylinder, and is separated from the electrolyte by an asbestos diaphragm E to prevent mechanical stirring of the liquid. Hydrogen is evolved at the cathode and escapes through the hydrogen outlet I. Chlorine is evolved at the anode surfaces, collects under the domelike top, and escapes through the chlorine outlet H. The sodium hydroxide formed in the electrolysis is drawn off at the bottom K of the cell

The chlorine set free in the electrolysis is either used directly at the place of preparation or compressed in strong steel cylinders (Fig. 103), loaded on cars, and shipped in this form (Fig. 102). Sometimes it is passed into slaked lime, making the solid known as *chloride of lime* or *bleaching*

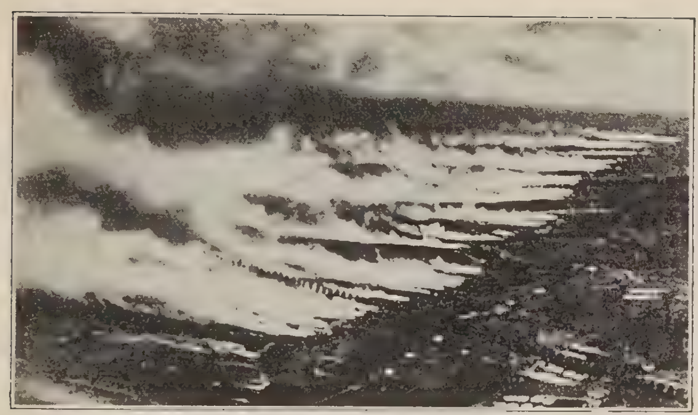


FIG. 100. Making a gas attack in Flanders

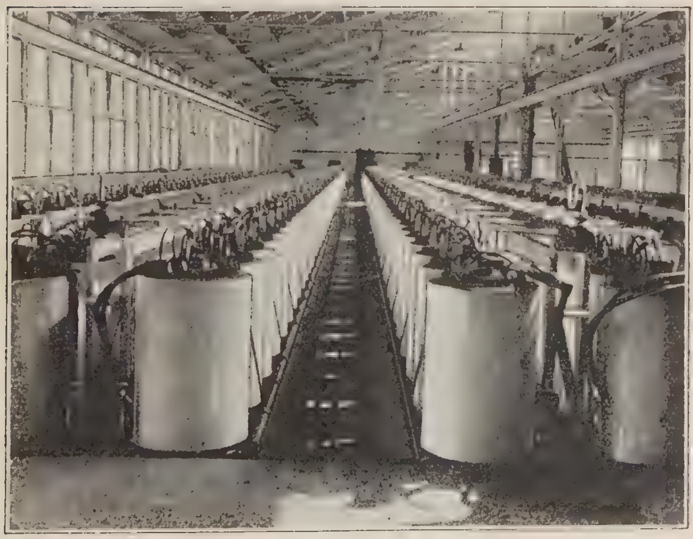


FIG. 101. A room filled with rows of Vorce cells

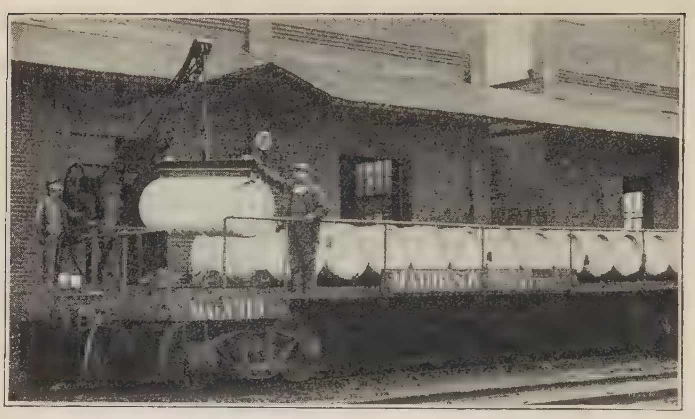


FIG. 102. Shipping a carload of 1-ton containers filled with liquid chlorine

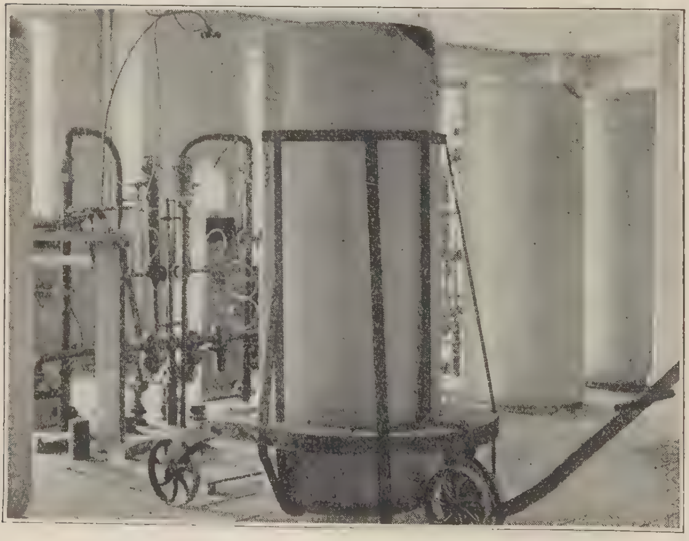


FIG. 103. Filling 1-ton containers with liquid chlorine

powder, which can easily be shipped and from which the chlorine can be recovered as needed.

The electrolytic method of preparation has the added advantage that the hydrogen and sodium hydroxide formed in the process along with the chlorine have many commercial uses. The chief item of expense is the cost of the electric current; for this reason the great center for preparing chlorine is at Niagara Falls, where water power is used for generating the current at a low cost.

212. Physical properties. Like oxygen and hydrogen, chlorine is a gas, but differs from them in many of its properties. It has a greenish-yellow color and a strong suffocating odor. One volume of water dissolves about 2.5 volumes of chlorine under ordinary laboratory conditions. It is much heavier than hydrogen or oxygen, being about 2.5 times as heavy as air.

Chlorine is rather easily condensed to a liquid. At ordinary temperatures (18°) it is liquefied by a pressure of 16.5 atmospheres. Since the commercial chlorine compressed in steel cylinders (or tank cars) for shipment is subjected to a much higher temperature than this, it is evident that the chlorine in these cylinders exerts a great pressure, though most of it is in a liquid state.

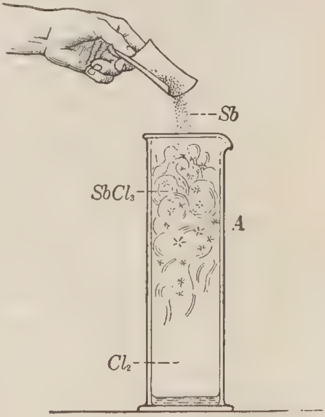


FIG. 104. Powdered antimony burning in chlorine

213. Chemical conduct. Chlorine is one of the most active of all the elements. It combines with all the metals, especially if they are hot, forming *chlorides* of the metals. A strip of hot copper foil dropped into a cylinder of chlorine burns brilliantly, forming chloride of copper ($CuCl_2$).

Antimony and arsenic in the form of a fine powder at once glow brilliantly when dropped into cylinders of chlorine (Fig. 104), forming the corresponding chlorides.

Chlorine is especially characterized by its affinity for hydrogen, the two uniting to form hydrogen chloride (HCl). A jet of hydrogen burning in air will continue to burn when introduced into a jar of chlorine, giving a somewhat luminous flame (Fig. 105). The two gases may be mixed in the dark without danger, but if an electric spark is passed through the mixture, or if it is exposed to the sunlight for an instant, a violent explosion takes place as the two elements combine.

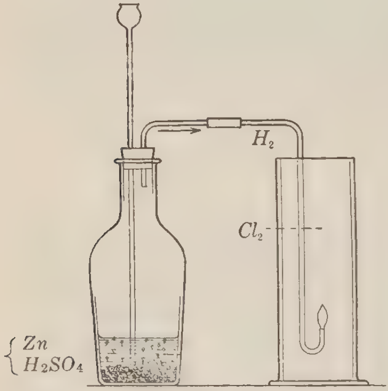


FIG. 105. Burning a jet of hydrogen in chlorine

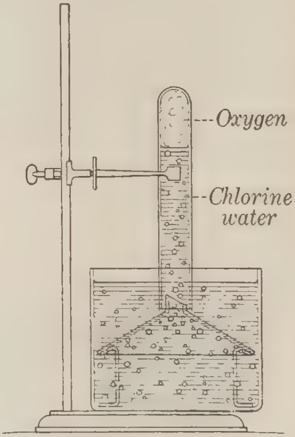


FIG. 106. Action of chlorine on water in strong sunlight

Chlorine will not only combine with hydrogen; it will take the hydrogen away from many of its compounds. A solution of chlorine in water will keep its strength for some time if kept in the dark, but in the sunlight the chlorine slowly combines with the hydrogen of the water, forming hydrogen chloride and liberating oxygen (Fig. 106). It is this property of chlorine that makes it so useful as a bleaching agent.

214. Valence of chlorine. It will be recalled that chlorine has a negative valence of 1. Its atom has seven electrons in its outer valence orbit, and has a strong tendency to capture one additional electron (Fig. 91). For this reason we should expect chlorine to combine with hydrogen and with the metals having small positive valences, and this is found to be the fact.

215. Uses of chlorine. Chlorine has many uses, but the two chief ones are (1) as a disinfectant and (2) as a bleaching agent. About five hundred tons of chlorine are produced daily for these uses.

1. ***Use as a disinfectant.*** In the chapter on water, mention was made of the presence of disease-producing bacteria in the water supply of our cities. Practically every city must purify its water supply, and chlorine is almost always used in the process. It is estimated that 3,000,000,000 gallons of water, or the equivalent of the volume of water that flows over the Niagara Falls in 44 seconds, are purified daily by the use of liquid chlorine. In this way typhoid fever has been greatly reduced (Fig. 42).

2. ***Use as a bleaching agent.*** The process known as *bleaching* is an important one in connection with many industries. The various kinds of fabrics woven from vegetable fibers, such as flax and cotton, are always more or less colored, and bleaching is necessary if a white fabric is desired. This was formerly accomplished by spreading the cloth on plots of grass and exposing it to the air and sunlight, but the process was a very slow one. The same results are now accomplished in a short time by the use of chlorine. Most of our paper is made from wood pulp, which must be bleached if a white paper is desired. The greatest single use of chlorine is in the bleaching of this wood pulp.

216. Why is chlorine a bleaching agent? If strips of bright-colored cloth or some highly colored flowers are placed in *dry* chlorine, no marked change in color is noticed, as a rule. If the cloth or flowers are first moistened with water, the color rapidly disappears (Fig. 107). Evidently the moisture as well as the chlorine is concerned in the action. Experiment shows that the chlorine sets the oxygen free from the water (§ 213), and the oxygen so liberated oxidizes the color substance (dye), converting it into a colorless compound. It is evident from this explanation that chlorine will bleach only such substances as are changed into colorless compounds by oxidation. It has no action on carbon, and hence does not affect printer's ink made from carbon black; and it must not be used for bleaching silk and straw, since it injures the fabric.

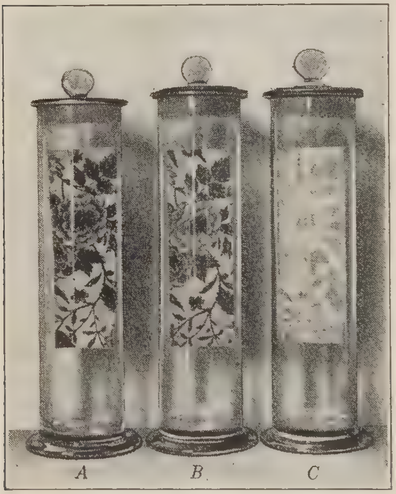


FIG. 107. Bleaching with chlorine

The jars *A*, *B*, *C* were filled with dry chlorine. The cloth in *A* was dry; in *B*, slightly moist; in *C*, thoroughly wet

217. Nascent state. It will be noticed that when oxygen is set free from water by chlorine it is at the instant of liberation much more active than ordinary oxygen; for it bleaches substances quickly, yet the same substances remain unchanged in pure air or oxygen — at least for a long time. Many elements other than oxygen have this increased activity while they are being set free from their compounds. To express this fact, elements at the instant of liberation are said to be in the *nascent state*, the word *nascent* being derived from a Latin word meaning "being born." When moist chlorine acts as a bleaching agent, it is the *nascent* oxygen that does the bleaching. This greater activity is usually accounted for by supposing that an element is liberated from its compounds in the form of atoms, and these are more active than after they have combined to form molecules, but we are not sure that this is the full explanation.

218. Hydrogen chloride (HCl). When hydrogen and chlorine combine, a colorless gas is formed, known as *hydrogen chloride.* This is a very important compound, since its solution in water constitutes *hydrochloric acid,* which has many commercial uses. The pure hydrogen chloride is 1.26 times as heavy as air. When inhaled it has an irritating and suffocating effect. It is very soluble in water; 1 volume of water, under standard conditions, dissolves a little more than 500 volumes of the gas. When exposed to moist air, hydrogen chloride gas attracts moisture, which condenses in minute droplets, forming little visible clouds or fumes.

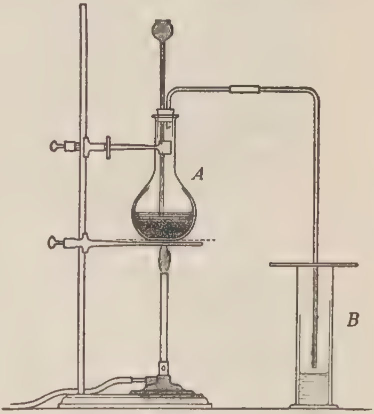


FIG. 108. The preparation of a solution of hydrogen chloride

219. Preparation. Hydrogen chloride can be prepared by burning hydrogen in chlorine (Fig. 105). It is much more convenient and much cheaper to prepare it by the action of sulfuric acid on sodium chloride. To prepare it by this method, the chloride is placed in the flask *A* (Fig. 108), and the flask is connected with stopper and tubes as shown in the figure. Sulfuric acid is added through the funnel tube *B* and the mixture gently heated. The two react as follows:

$$2\,NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2\,\overline{HCl}$$

The sodium sulfate remains in the flask, while the hydrogen chloride escapes through the exit tube and can be collected by displacement of air, as in the case of chlorine (Fig. 98). To prepare a solution of the gas, the end of the delivery tube is fixed *just above* the level of some water in the cylinder *B*. The gas, being very soluble, dissolves in the water as fast as it escapes from the tube.

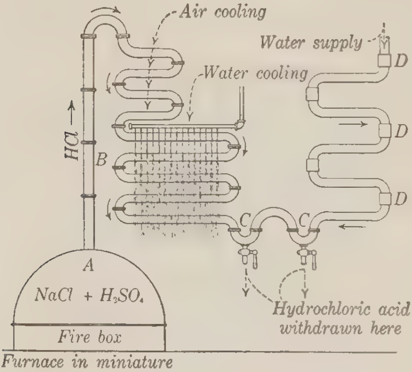


FIG. 109. Commercial preparation of hydrochloric acid

Sodium chloride and sulfuric acid are heated together in the furnace *A*, and the resulting hydrogen chloride escapes through the pipe *B*. It is first air-cooled, then water-cooled, and finally absorbed in water in the traps *C*. Water is renewed from time to time through *D*

On a commercial scale the sodium chloride and sulfuric acid are heated together in large furnaces (Fig. 109). The hydrogen chloride formed is absorbed in water, forming the *hydrochloric acid* of commerce. This product always contains some impurities; the impure product is often called *muriatic acid.*

220. The properties and chemical conduct of hydrochloric acid. Pure hydrochloric acid is a colorless liquid. The density of this liquid increases with the amount of hydrogen chloride dissolved. The ordinary concentrated acid used in our laboratories has a density of about 1.2 and contains a little more than 40 per cent by weight of hydrogen chloride.

It is interesting to know that a small percentage of hydrochloric acid is present in the gastric juice secreted by the glands in the stomach and is an important factor in the digestion of our food.

Hydrochloric acid is one of our most common and most useful laboratory reagents. Some of its important properties are the following:

1. ***Taste.*** A dilute solution of the acid has a sour taste like that of vinegar.

2. ***Action on colored compounds.*** It acts upon many colored compounds and changes their color in some way — very often to a red. Thus it changes the blue color of litmus to red. Litmus is a coloring matter obtained from a plant.

3. ***Action upon metals and their hydroxides.*** When hydrochloric acid is brought into contact with certain metals or their hydroxides, the hydrogen of the acid is replaced by the metal forming a *chloride*, thus:

$$\begin{aligned} 2\,\mathrm{Na} + 2\,\mathrm{HCl} &\longrightarrow 2\,\mathrm{NaCl} + \mathrm{H_2} \\ \mathrm{NaOH} + \mathrm{HCl} &\longrightarrow \mathrm{NaCl} + \mathrm{HOH}\ (\mathrm{H_2O}) \\ \mathrm{Zn} + 2\,\mathrm{HCl} &\longrightarrow \mathrm{ZnCl_2} + \mathrm{H_2} \\ \mathrm{Zn(OH)_2} + 2\,\mathrm{HCl} &\longrightarrow \mathrm{ZnCl_2} + 2\,\mathrm{H_2O} \end{aligned}$$

221. Test for hydrochloric acid and chlorides. Suppose we wish to know whether a certain liquid is hydrochloric acid or contains some hydrochloric acid along with other substances. The liquid might be water or alcohol or any number of compounds dissolved in water. What reaction or *test* can we apply to the liquid that will tell us whether hydrochloric acid is present? The test commonly used is the following:

We pour some of the liquid into a test tube, add a few drops of nitric acid, and then two or three drops of a solution of silver nitrate ($AgNO_3$). If hydrochloric acid is present, a white precipitate of silver chloride ($AgCl$) is at once formed in accordance with the following equation:

$$\mathrm{AgNO_3} + \mathrm{HCl} \longrightarrow \underline{\mathrm{AgCl}} + \mathrm{HNO_3}$$

The nitric acid added in making the test prevents the silver nitrate from forming a white precipitate with certain other compounds that might be present.

Solutions of chlorides of metals, such as a solution of sodium chloride in water, will likewise give a precipitate of silver chloride, thus:

$$AgNO_3 + NaCl \longrightarrow \underline{AgCl} + NaNO_3$$

The formation of the white precipitate under the above conditions tells us, then, that either hydrochloric acid or a chloride is present. It is a simple matter, however, to distinguish between hydrochloric acid and a chloride. For example, hydrogen is evolved when a bit of zinc is added to hydrochloric acid, but not when added to a solution of a chloride.

222. Commercial compounds; chemically pure compounds; by-products. The product first obtained in the preparation of any compound, especially on a large scale, is certain to contain impurities. We generally designate this as the *commercial* product. When these impurities are all removed the compound is designated as *chemically pure*, or simply C. P. The commercial product serves just as well as the chemically pure for many purposes and is much cheaper.

It is generally true that in the preparation of any substances by chemical processes, there is formed other substances along with the main product. *The substances obtained in any process aside from the main product are called by-products.* Thus in the laboratory method for preparing hydrogen (§ 60, 2), zinc sulfate is a by-product; likewise in the manufacture of charcoal (§ 159, 2), methanol (wood alcohol) and acetic acid are by-products. The commercial success of many processes depends upon the value of the by-products formed.

CHAPTER SUMMARY IN QUESTION FORM

1. (*a*) When and by whom was chlorine discovered? (*b*) Why was it named chlorine?

2. Where do we find chlorine (*a*) in the free state? (*b*) in the combined state?

3. (*a*) What is the most abundant compound of chlorine? (*b*) How do we liberate the chlorine from this compound in the laboratory?

4. Supply the missing words in the following: Chlorine has a ------ odor, is soluble in ------, reacts slowly with water, and explodes violently when mixed with ------ in direct sunlight. Its most important uses are to purify ------, and to ------ cloth and ------.

5. (*a*) From what compound is chlorine prepared commercially, and by what process? (*b*) Name two other substances prepared at the same time.

6. Compare chlorine and oxygen as to (*a*) weight; (*b*) color; (*c*) odor; (*d*) solubility in water; (*e*) effect when breathed.

7. Is the chlorine that we buy in cylinders in the form of a gas, a liquid, or a solid?

8. What name is given to a compound formed by the union of chlorine with another element?

9. A jet of hydrogen burning in air will continue to burn when the flame is lowered into a jar of chlorine. Name the compound formed when the hydrogen burns (*a*) in air; (*b*) in chlorine.

10. (*a*) Name four elements that combine readily with chlorine. (*b*) Name the compound formed in each case.

11. Name the two important uses of chlorine.

12. How do we explain the fact that chlorine will not bleach unless water is present?

13. (*a*) What name do we apply to the state of an element at the instant of its liberation from a compound? (*b*) How do we account for the greater activity of the element when in this state?

14. (*a*) Name two ways of getting hydrogen chloride. (*b*) Which of these is the cheaper? (*c*) Describe the method used for preparing hydrogen chloride on a commercial scale.

15. How do we distinguish in name between gaseous HCl and its solution in water?

16. Complete and balance the following equations:

$$NaCl + H_2SO_4 \longrightarrow$$
$$Zn + HCl \longrightarrow$$

17. Fill in the vacant places with the right words: Hydrochloric acid is a solution of ------ ------ in ------. It has a ------ taste, colors ------ litmus ------, and contains ------ which can be replaced by some metals such as ------.

18. How can you test a solution for the presence (*a*) of hydrochloric acid? (*b*) of a chloride?

19. (*a*) What is meant by the term *by-product*?

THOUGHT QUESTIONS

1. What elements so far studied are found (*a*) free in nature? (*b*) combined? (*c*) both free and combined?

2. Account for the fact that some elements are found free in nature while others are not.

3. Why do we use one method for the preparation of chlorine in the laboratory and another for preparing it on a large scale?

4. (*a*) How does the weight of chlorine compare with the weight of an equal volume of each of the other common gases? (See page facing back cover.) (*b*) Calculate its density as compared with the density of each of the other gases so far studied.

5. How many electrons are there in the outer (or valence) orbit of the atom of (*a*) chlorine? (*b*) hydrogen? (*c*) oxygen? (*d*) Why should you expect hydrogen to combine with chlorine?

6. Very serious trouble would result if you attempted to collect hydrogen chloride over water in the laboratory preparation of this gas. Explain.

7. Since you cannot collect hydrogen chloride over water, and since the gas is invisible, how can you tell when the bottle in which you are collecting the gas is filled?

8. (*a*) In the process of preparing hydrogen chloride in the laboratory, what four compounds (aside from water) are present in the flask? (*b*) Why do some of the products leave the flask while others remain in it?

9. (*a*) What is the percentage of chlorine in sodium chloride? (*b*) What weight of sodium chloride would be required in the preparation of 10 tons of chlorine?

10. Suppose you wished to prepare 1 liter of chlorine in order to study its properties. What weight of (*a*) manganese dioxide and of (*b*) hydrogen chloride would be required?

11. (*a*) Write the equation for the reaction that takes place when hydrogen and chlorine combine to form hydrogen chloride. What is the ratio (*b*) between the volumes of hydrogen and chlorine that combine with each other? (*c*) between the volume of either one and that of the hydrogen chloride formed? (Solve (*b*) and (*c*) by application of Avogadro's law (§ 173).)

FOR HONOR STUDENTS

1. Design and exhibit to the class a small model showing the principal parts of a Vorce cell for the production of chlorine.

2. Laboratory supply houses sell concentrated hydrochloric acid in bottles containing $2\frac{1}{2}$ liters of the acid. This acid has a density of 1.2. (*a*) Calculate the weight of the liquid. (*b*) Calculate the weight of hydrogen chloride in the liquid (§ 220). (*c*) What weight of sodium chloride would be required to prepare this weight of hydrogen chloride?

CHAPTER XVI

SODIUM AND POTASSIUM

Metals that are Lighter than Water

223. ***Introduction.*** We are all inclined to judge persons and things by their looks, yet we know that this is not a very sound basis for judging. An automobile may be very beautiful, but if it will not run it is of no use. The crucial test is not so much how a thing looks as how it acts. The alchemists classified substances according to their physical properties, and so we find them including sulfuric acid and olive oil in the same class because they look alike, although they are unlike in nearly every other respect. Chemists now classify elements and compounds not according to their looks but according to their chemical actions.

Anyone who has never studied chemistry thinks of a metal as something heavy, hard, and not easily melted, and in the main this idea is correct. Yet the two metals which we are now to study are so light that they float on water, so soft that they can easily be molded by the fingers, and they melt below the boiling point of water. Nevertheless, as we proceed with our study we shall find that they possess those chemical properties that are characteristic of the metals.

224. The discovery of sodium and potassium. Sodium forms sodium hydroxide ($NaOH$), and potassium forms the similar compound, potassium hydroxide (KOH). These hydroxides are white solids, and are often sold in the form of sticks (Fig. 113). They have long been known, and were at first regarded as elements. In 1807 the English chemist

Humphry Davy (Fig. 110), knowing that water could be decomposed by the electric current, tried the effect of the current on these hydroxides, thinking he might be able to decompose them also into simpler substances. He first experimented with potassium hydroxide, and found, as he states, that "small globules having a high metallic luster similar in visible character to quicksilver appeared." This was the first preparation of the element we now call potassium. A few days later he carried out a similar experiment with sodium hydroxide and obtained sodium.

FIG. 110. Sir Humphry Davy (1778-1829)

A distinguished English scientist who proved that chlorine is an element and first isolated the elements sodium and potassium

225. Occurrence. Both sodium and potassium are very active elements, so that we should not expect to find them free in nature. If set free in any way, they would at once combine with oxygen or react with water. Their compounds, however, might be very abundant, and in fact they are present in all natural waters and in most rocks. Sodium chloride is the most abundant of all these compounds. Not only is it present in all salt waters, but the solid compound occurs in many localities, and is mined much as coal is mined (Fig. 111). Among other compounds of sodium found in nature are borax, sodium carbonate, and sodium nitrate. The nitrate occurs in large deposits in Chile, and is sometimes known commercially as *Chile saltpeter*.

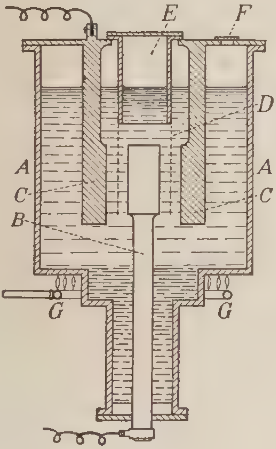
Large deposits of nearly pure potassium compounds are found in certain localities in Germany and France, where they are mined and shipped to the United States and used as a fertilizer; for potassium compounds are necessary for the growth of plants, and our production of them is small.

226. Preparation. We prepare sodium and potassium today just as Davy prepared them, namely, by the electrolysis of their hydroxides. Naturally we have greatly improved the details of the method. The current of electricity is passed through melted hydroxides. All water must be excluded; otherwise the metals would react with the water as fast as they were liberated, and we should get not the free metals but their hydroxides. In the case of sodium the preparation is carried out as shown in Fig. 112. Potassium is prepared in a similar way, but the process is more difficult to carry out. As a result potassium costs more than sodium and is but little used. Sodium has a limited use in the preparation of certain compounds.

FIG. 111. Mining salt

A mechanical loader at work in a salt mine

227. Properties and chemical action of sodium and potassium. These two elements resemble each other very closely. They not only look alike but they act alike, so that for almost every purpose for which they are used either one can be employed. They are soft, light, and easily melted. When pure they have a bright luster like silver, and in this respect resemble the more familiar metals.



Sodium hydroxide is melted in a cylindrical iron vessel *A*, through the bottom of which rises the cathode *B*. The anodes *C*, several in number, are suspended around the cathode from above. A cylindrical vessel *E* floats in the fused alkali, directly over the cathode, and under this cap the sodium and hydrogen liberated at the cathode collect. The hydrogen escapes by lifting the cover, and the sodium, protected from the air by the hydrogen, is from time to time skimmed or drained off. Oxygen is set free upon the anode and escapes into the air through the opening *F* without coming into contact with the sodium or the hydrogen

FIG. 112. A Castner cell for the electrolytic production of sodium

We have already learned that sodium displaces hydrogen from water (§ 60, 1). Potassium acts in the same way, only more vigorously. They likewise displace hydrogen from acids (§ 220, 3), and the chief reason we use zinc in place of sodium or potassium in preparing hydrogen (§ 60, 2) is because the zinc is far cheaper and the action is more readily controlled. Because of their great affinity for oxygen, they almost instantly tarnish when exposed to the air; hence we preserve them by keeping them immersed in kerosene, since they do not act on this liquid.

228. Valence of sodium and of potassium. Like hydrogen, both sodium and potassium have but one valence electron, and are therefore positive univalent elements. They give up their valence electrons even more readily than does hydrogen, and it is for this reason that they displace hydrogen from water and acids. Thus, in the reaction

$$2\,Na + 2\,HOH \longrightarrow 2\,NaOH + H_2$$

a hydrogen atom in the water molecule, which has given its valence electron to the oxygen atom, recovers it from the sodium atom, which then replaces the hydrogen atom in the water molecule. The free hydrogen atoms then combine to form molecules (H_2).

229. Sodium hydroxide (caustic soda) (NaOH). Someone has said that the state of civilization of a nation can be told from the amount of soap it uses, and hence from the amount of sodium hydroxide it uses; for this is used in the manufacture of nearly all our soaps. In addition we use it in making paper and in refining petroleum. In the laboratory it is one of our common reagents. This compound, then, is of very great importance.

SODIUM
HYDROXIDE

FIG. 113. The form of sodium hydroxide most familiar in the laboratory

Sodium hydroxide (Fig. 113) is a very active compound, and when exposed to the air it rapidly absorbs moisture and carbon dioxide from the air. It is very soluble in water, and it is this solution that is commonly used. When brought into contact with the skin it acts as a caustic; that is, it burns or corrodes the skin; hence the name *caustic soda* which is often applied to this compound. As an article of household use it is called *lye*.

230. Preparation. Sodium hydroxide is prepared commercially by two different processes, as follows:

1. In the older process sodium carbonate is treated in solution with calcium hydroxide (slaked lime, § 168). Calcium carbonate is precipitated as an insoluble solid, according to the equation

$$Na_2CO_3 + Ca(OH)_2 \longrightarrow \underline{CaCO_3} + 2\,NaOH$$

The dilute solution of sodium hydroxide, filtered from the insoluble calcium carbonate, is evaporated to dryness; the solid is then melted and poured into molds to solidify. Most of the sodium hydroxide is made by this method.

2. The newer method consists of the electrolysis of a solution of sodium chloride as explained under chlorine (§ 211). Every chlorine plant is, therefore, a plant for producing sodium hydroxide.

231. Potassium hydroxide (caustic potash) (KOH). Potassium hydroxide is prepared in the same way as sodium hydroxide, and resembles it closely in properties. Since the sodium hydroxide is cheaper, it is more widely used.

232. Chemical conduct. Both sodium hydroxide and potassium hydroxide have certain properties in common with the hydroxides of many other metals. These common properties are as follows:

1. ***Action on litmus.*** Their solutions act on litmus (as well as on certain other colored substances) in just the opposite way from the acids (§ 220, 2); that is, they turn red litmus blue.

2. ***Action on acids.*** When brought into contact with acids, the metal of the hydroxide changes places with the hydrogen of the acids, thus:

$$NaOH + HCl \longrightarrow NaCl + HOH\ (H_2O)$$
$$KOH + HCl \longrightarrow KCl + HOH\ (H_2O)$$

In the following chapter we shall find that these hydroxides belong to a very important class of compounds called *bases*.

CHAPTER SUMMARY IN QUESTION FORM

1. (*a*) Who discovered sodium and potassium? (*b*) What fact suggested the experiment which led to their discovery?

2. Name three important compounds of sodium found in nature.

3. (*a*) Where do we find large deposits of potassium compounds? (*b*) What is the chief use of these compounds?

4. (*a*) Give the method for preparing sodium and potassium. (*b*) Which is the more difficult to prepare?

5. (*a*) In what respects does sodium resemble silver in physical properties? (*b*) In what respects does it differ?

6. How can sodium hydroxide be prepared (*a*) from sodium chloride? (*b*) from sodium carbonate?

7. By what other name is sodium hydroxide known (*a*) in the chemical laboratory? (*b*) in our homes?

8. What is the chief use of sodium hydroxide?

9. Fill in the missing words in the following: Sodium hydroxide and potassium hydroxide are ______ solids. Their solutions in water turn ______ litmus ______. When they are brought in contact with acids, the ______ of the hydroxide exchanges places with the ______ of the acids.

THOUGHT QUESTIONS

1. Write the equations for the reaction of sodium on each of the following: (*a*) water; (*b*) sulfuric acid; (*c*) hydrochloric acid; (*d*) oxygen (formula for oxide formed, Na_2O_2).

2. (*a*) Explain why water must not be present in the preparation of sodium. (*b*) Name two substances that would be formed in case water were present.

3. (*a*) Which are the more important commercially, sodium and potassium or their compounds? (*b*) Give the reason for your answer.

4. An industrial plant that prepares sodium carbonate is very likely to prepare sodium hydroxide also. Explain.

5. What two properties has kerosene that make it suitable for preserving sodium?

6. Calculate from their formulas the molecular weights of (*a*) sodium hydroxide and (*b*) potassium hydroxide. In a given chemical reaction which would go farther, 100 lb. of sodium hydroxide or 100 lb. of potassium hydroxide?

7. Suppose you wished to prepare 100 lb. of sodium hydroxide by the older method. (*a*) What compounds would you need? (*b*) Calculate the weight of each that would be required.

FOR HONOR STUDENTS

1. About 500 tons of chlorine are prepared daily in the United States; what weight of sodium hydroxide is formed in the process?

2. From Fig. 114 construct a model of the apparatus used in the commercial preparation of sodium. The outside of the cell is cut from a bottle of suitable size as follows: Around the bottle at the place you wish to cut it, wrap some candle wick soaked in alcohol. Ignite the alcohol, let it burn for ten or fifteen seconds, and immerse the entire bottle in cold water.

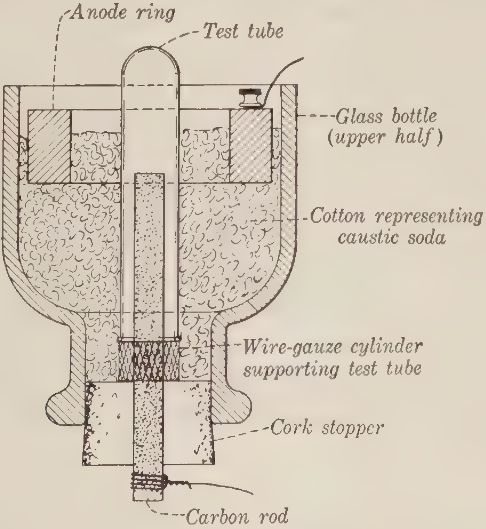

Anode ring
Test tube
Glass bottle (upper half)
Cotton representing caustic soda
Wire-gauze cylinder supporting test tube
Cork stopper
Carbon rod

FIG. 114. Model of a Castner cell

CHAPTER XVII

ACIDS, BASES, AND SALTS

The Three Most Important Groups of Compounds

233. *Introduction.* We have learned that chemists have good reason for believing that there are ninety-two elements. Of this number ninety are known. The number of compounds that can be made up of different combinations of two or more of these elements is almost unlimited (§ 24). If all these compounds were entirely different from each other, and each one had to be studied by itself, the task would be hopeless. Fortunately they fall into certain classes or groups, and by studying the characteristics of a group we can obtain a general knowledge of each member of the group.

Most of the compounds which we shall study in this text belong to one of three groups, *acids*, *bases*, and *salts*. Having now studied a typical acid (hydrochloric acid) and a typical base (sodium hydroxide and potassium hydroxide), we shall proceed to study these groups as a whole. And to these groups we shall add the third group, salts, which is made up of compounds formed when an acid and a base act on each other.

234. Acids. In addition to hydrochloric acid, we are constantly using in our laboratories at least two other common acids, sulfuric acid and nitric acid (Fig. 115). Sulfuric acid is a solution in water of an oily, colorless liquid called hydrogen sulfate (H_2SO_4) ; nitric acid is a solution in water of a colorless liquid known as hydrogen nitrate (HNO_3). For most purposes it is not necessary to distinguish between these compounds and their solutions in water, and both are frequently called acids. The properties that are characteristic of acids, however, appear only when water is present (or some other liquid that acts like water).

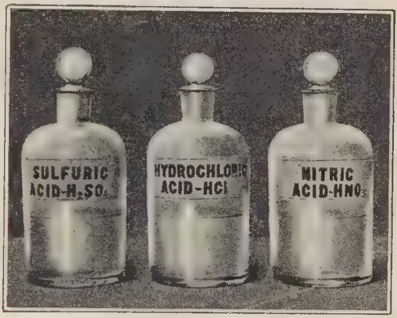


FIG. 115. The three common acids

The characteristic properties of acids are in the main those given for hydrochloric acid (§ 220). We may therefore define an acid as follows:

An acid is a compound of hydrogen whose solution in water (1) has a sour taste, (2) changes blue litmus to red, and (3) acts on metals and their hydroxides, forming compounds in which the hydrogen atoms of the acid are replaced by atoms of the metal.

Just as the students in a class have many characteristics in common and yet may differ widely in certain traits, so the acids, although possessing many common properties, may differ in other properties. Thus, some acids are very stable, others are easily decomposed; some have a marked odor, others are odorless; some are very poisonous, others are harmless and may even be useful as food. Vinegar contains acetic acid, apples and pears contain malic acid, and oranges and grapefruit contain citric acid.

235. Bases. The hydroxides of the metals are known as *bases.* Some of these are very soluble in water, as is the case with sodium hydroxide and potassium hydroxide; others, like calcium hydroxide ($Ca(OH)_2$), are only slightly soluble; while others, like aluminum hydroxide ($Al(OH)_3$), are insoluble. Those that are soluble act on litmus (and certain other colored substances) in just the opposite way from acids; that is, their solution turns red litmus blue. The most characteristic property of the bases is their action on acids. When a base and an acid are brought into contact, the hydrogen atoms of the acid are replaced by the metal atoms of the base, thus:

$$NaOH + HCl \longrightarrow NaCl + HOH\ (H_2O)$$

We may now define a base as follows:

A base is a compound of a metal and one or more OH groups, the number depending on the valence of the metal. It reacts with an acid, forming a compound in which the hydrogen atoms of the acid are replaced by the metal atoms of the base. If it is soluble in water, the solution turns red litmus blue.

236. Alkalies. Those bases that are freely soluble in water have the most highly developed basic properties, and are often called *alkalies*. The common alkalies are sodium hydroxide and potassium hydroxide.

237. Salts; neutralization. We have seen that when an acid and a base are brought together, a reaction takes place which consists in the interchange of the hydrogen atoms of the acid with the atoms of the metal of the base. The following will serve as examples:

$$HCl + NaOH \longrightarrow NaCl + HOH$$
$$2\ HCl + Ca(OH)_2 \longrightarrow CaCl_2 + 2\ HOH$$
$$H_2SO_4 + 2\ NaOH \longrightarrow Na_2SO_4 + 2\ HOH$$

In all such reactions as these, the acid and the base are said to *neutralize* each other, and the compound formed, other than water, is called a *salt*. An examination of the formulas of the salts will show that they differ in composition from the acids in that the molecules of the salt contain a metal in place of hydrogen. We may define a salt as follows:

A salt is a compound derived from an acid by replacing the hydrogen atoms of the acid by the atoms of a metal.

238. Number of salts. From what has been said, we should expect that each acid would form as many salts as there are metals, and this is, in general, true. In a few cases the expected salt cannot be prepared, but the number of salts that may be derived from any acid is apt to be large. The following equations represent the formation of a number of typical salts derived from sulfuric acid:

$$H_2SO_4 + 2\ NaOH \longrightarrow Na_2SO_4 + 2\ H_2O$$
$$H_2SO_4 + Ca(OH)_2 \longrightarrow CaSO_4 + 2\ H_2O$$
$$H_2SO_4 + Fe(OH)_2 \longrightarrow FeSO_4 + 2\ H_2O$$
$$H_2SO_4 + Cu(OH)_2 \longrightarrow CuSO_4 + 2\ H_2O$$
$$3\ H_2SO_4 + 2\ Al(OH)_3 \longrightarrow Al_2(SO_4)_3 + 6\ H_2O$$

239. Indicators. We have seen that acids turn blue litmus to a red color, while bases reverse the change, turning red back to blue. We may employ litmus, therefore, to determine whether a given solution is acid or basic. It may also be used to determine whether or not a solution is *neutral* (that is, neither acid nor basic), for such solutions will have no effect on either blue or red litmus. In addition to litmus, certain other colored compounds may be used for determining whether solutions are acid, basic, or neutral; and all these are known collectively as *indicators*. Some blue flowers and red fruit juices may be used as indicators.

240. Radicals. When we study the formulas of the molecules of various compounds, we sometimes notice a group of two or more atoms that seem to keep together and form a natural unit within a molecule.

For example, if we compare the formulas H_2SO_4, Na_2SO_4, $CuSO_4$, it will be seen that they all contain the group of atoms SO_4. Similarly, all the bases, illustrated by the formulas NaOH, KOH, contain the group of atoms OH. *A group of atoms which act together as a unit in chemical reactions is called a radical.* The group SO_4 is called the *sulfate radical*; the group OH is called the *hydroxyl radical.*

241. Valence of radicals. Radicals, like atoms, have valence; that is, they tend to gain or lose electrons. We may infer the valence of a radical from the formulas of the compounds in which the radical is present, just as we may infer the valence of an atom. The hydroxyl radical is univalent, as is shown by the formulas NaOH, KOH, HOH, the atoms Na, K, and H being univalent. The sulfate radical (SO_4) is bivalent, as is shown by the formulas H_2SO_4, Na_2SO_4, $CuSO_4$; for it combines with two univalent atoms (H or Na) or with one bivalent atom (Cu).

COMMON RADICALS WITH THEIR VALENCES

NAME	FORMULA	VALENCE
Ammonium radical	NH_4	+ 1
Nitrate radical	NO_3	− 1
Hydroxyl radical	OH	− 1
Carbonate radical	CO_3	− 2
Sulfate radical	SO_4	− 2
Phosphate radical	PO_4	− 3

242. Formulas of molecules containing radicals. In the formula of a compound it is desirable to indicate *the radical* as a part of the compound just as we indicate the various *atoms*. Calcium is a bivalent element, so we write the formula of its hydroxide $Ca(OH)_2$ (corresponding to its chloride, $CaCl_2$) rather than CaO_2H_2, which does not suggest the radical OH. Aluminum is a trivalent element, and we write the formula of its hydroxide $Al(OH)_3$ rather than AlO_3H_3. The formula of its sulfate is written $Al_2(SO_4)_3$ rather than $Al_2S_3O_{12}$.

243. Formulas of salts. When we know the valence of a metal and the formula of any acid and thus the valence of its radical, it is easy to deduce the formula of the salt which the metal may naturally be expected to form with the acid. Thus, suppose we wish to write the formulas of the salt which the bivalent metal calcium forms with the acids HCl, H_2SO_4, and H_3PO_4 respectively. First write the symbol of the element in place of the hydrogen of the acid:

$$CaCl \qquad CaSO_4 \qquad CaPO_4$$

Now write over the symbols of calcium, chlorine, and each of the radicals SO_4 and PO_4 the valence of each element or radical:

$$\overset{2}{Ca}\overset{1}{Cl} \qquad \overset{2}{Ca}\overset{2}{SO_4} \qquad \overset{2}{Ca}\overset{3}{PO_4}$$

Finally, take such numbers of the two constituents of each salt as will add up an equal number of valences. This gives the following as the correct formulas:

$$CaCl_2 \qquad CaSO_4 \qquad Ca_3(PO_4)_2$$

244. How acids, bases, and salts are named. It would be very convenient for us oftentimes if we had some way of knowing a person's name, even though we may never have met the person before. Unfortunately this is impossible. Chemists are able to do somewhat better in reference to compounds; for they have framed certain rules for naming compounds, including the acids, bases, and salts, so that if we are given the formula of a compound we can generally tell whether it belongs to any one of these three groups, and if so, its name. The rules which chemists have agreed upon for naming these compounds are as follows:

1. ***Acids.*** All the common acids contain either two elements or three elements. Those that contain but two elements are called *binary acids* and are given names consisting of the prefix *hydro-* (abbreviation for "hydrogen"), the name of the second element present (abbreviated if necessary), and the termination *-ic.* Examples: HCl, hydrochloric acid; H_2S, hydrosulfuric acid.

Acids that contain three elements are called *ternary acids.* Most of these contain oxygen in addition to hydrogen, and it is the element other than hydrogen and oxygen that gives its name to the acid. Thus, it is the chlorine in

$HClO_3$ that gives its name to the acid, and the sulfur in H_2SO_4. It usually happens that the same three elements can unite in different proportions to form two or more acids. The most familiar one of these is given a name ending in *-ic*. For example, $HClO_3$ is called chloric acid, and H_2SO_4 sulfuric acid. The acid containing one less atom of oxygen than the *-ic* acid is given the termination *-ous*. If more than two acids are known, use is made of the prefixes *per-*, signifying "more," and *hypo-*, signifying "less." Examples:

Acid	Formula	Acid	Formula
Hypochlorous	$HClO$	Hyposulfurous	H_2SO_2
Chlorous	$HClO_2$	Sulfurous	H_2SO_3
Chloric	$HClO_3$	Sulfuric	H_2SO_4
Perchloric	$HClO_4$	Persulfuric	H_2SO_5

2. ***Bases.*** All bases have the common name *hydroxides*. They are distinguished from each other by using the name of the metal present. Example: $NaOH$, sodium hydroxide; $Ca(OH)_2$, calcium hydroxide.

3. ***Salts.*** A salt derived from a binary acid is given a name consisting of the names of the two elements composing it, with the termination *-ide*. Example: $NaCl$, sodium chloride.

A salt of a ternary acid is named in accordance with the acid from which it is derived. A ternary acid with the termination *-ic* gives a salt with the name ending in *-ate*, while an acid with the termination *-ous* gives a salt with the name ending in *-ite*. The following table, giving a number of examples, will make the application of these principles clear:

Acid	Formula	Sodium Salt	Formula
Hydrochloric	HCl	Sodium chloride	$NaCl$
Hypochlorous	$HClO$	Sodium hypochlorite	$NaClO$
Chlorous	$HClO_2$	Sodium chlorite	$NaClO_2$
Chloric	$HClO_3$	Sodium chlorate	$NaClO_3$
Perchloric	$HClO_4$	Sodium perchlorate	$NaClO_4$

245. Carbonic acid and its salts, the carbonates. We learned in our study of carbon dioxide that when this gas is passed into water a little of it combines with the water to form the compound H_2CO_3, known as *carbonic acid* (§ 168). Since we have now learned the characteristics of acids and salts, it is important for us to know something further about carbonic acid and its salts. The acid itself is very unstable, so that it can be obtained only in dilute solution; but its salts, known as the *carbonates*, are stable solids, some of which are very useful. Thus, limestone is mainly calcium carbonate ($CaCO_3$), while white marble is nearly pure calcium carbonate. Ordinary baking soda and washing soda are sodium salts of this acid.

When a carbonate is treated with an acid such as hydrochloric acid, carbon dioxide is given off (§ 165). This reaction serves as a simple test for the carbonates. It is only necessary to add a few drops of hydrochloric acid to the compound being tested, and conduct any gas evolved through some limewater. If the compound is a carbonate, then carbon dioxide is given off, and this causes a white precipitate of calcium carbonate in the limewater (§ 168).

CHAPTER SUMMARY IN QUESTION FORM

1. Most of the compounds we shall study belong to one of three groups. Name these groups.

2. (*a*) Name three common acids and (*b*) give their formulas.

3. Name the element common to all acids.

4. State three properties common to all acids.

5. Name three ways in which acids may differ from each other.

6. What name do we give to the hydroxide of a metal?

7. Name three properties common to all soluble bases.

8. By what other name are the more soluble bases known?

9. Write the formula for (*a*) an important acid; (*b*) an important base. (*c*) Now write the equation for the reaction that will take place when these two compounds are brought together.

10. Fill in the missing words in the following: When an acid and a base react together, they are said to ______ each other, and there is formed ______ and a compound known as a ______.

11. The hydrogen of an acid is replaced by a metal. To what group does the resulting compound belong?

12. In general, how many salts can be derived from any one acid?

13. How can we tell whether a given liquid is (*a*) acid, (*b*) basic, or (*c*) neutral?

14. What word do we give to a group of atoms that act together as a unit in a chemical reaction?

15. (*a*) Name each of the following groups of atoms: OH, SO_4, NO_3. (*b*) How can you determine the valence of each of these groups?

16. How many elements are present in (*a*) a binary acid? (*b*) a ternary acid?

17. Illustrate the method of naming binary acids by giving the names of the following: (*a*) HCl; (*b*) H_2S; (*c*) HBr.

18. (*a*) Name the two elements that are present in most ternary acids. (*b*) Which one of the elements present in a ternary acid gives its name to the acid?

19. State what element gives its name to each of the following acids: (*a*) H_2SO_4; (*b*) H_3PO_4; (*c*) H_2CO_3.

20. Distinguish by name between the following acids: H_2SO_4 and H_2SO_3; $HClO_3$ and $HClO_4$.

21. What word is common to the names of all bases?

22. Name the following salts, and tell how each name is derived: $NaCl$, KCl, Na_2SO_4, $ZnSO_4$.

THOUGHT QUESTIONS

1. Classify the compounds represented by the following formulas as acid, base, or salt: HCl, $NaNO_3$, K_2SO_4, HNO_3, $CaCl_2$, $Pb(NO_3)_2$, H_2SO_4, $Al_2(SO_4)_3$, KOH, $Cu(OH)_2$.

2. Predict the number of salts that might be formed from two acids and ten metals.

3. State the effect of each of the following on both colors of litmus paper: (*a*) hydrochloric acid; (*b*) a solution of sodium hydroxide; (*c*) a solution made by bringing together an equal number of molecules of hydrochloric acid and sodium hydroxide.

4. Copy the following table and write under the formula of each base, and opposite the formula of each acid, the formula of the salt formed by the action of the acid on the base:

	$NaOH$	$Ca(OH)_2$	$Al(OH)_3$
HCl			
HNO_3			
H_2SO_4			

5. Write the formulas for the salts formed by the action of the three common acids (Fig. 115) on each of the following metals: Na (univalent), Ca (bivalent).

6. Complete and balance the following equations:

$$HNO_3 + NaOH \longrightarrow \qquad H_2SO_4 + KOH \longrightarrow$$

$$HCl + Ca(OH)_2 \longrightarrow \qquad H_2SO_4 + Ba(OH)_2 \longrightarrow$$

7. Calculate the weight of hydrogen chloride necessary to neutralize 50 g. of sodium hydroxide.

8. Suppose that after neutralizing the sodium hydroxide in problem 7, you evaporated the solution to dryness. (*a*) What compound would be left? (*b*) Calculate its weight.

FOR HONOR STUDENTS

1. Test samples of common substances, such as those listed, to see whether their solutions are acid, basic, or neutral in reaction: vinegar; washing soda; borax; sugar; tooth paste; baking soda; cream of tartar; lemon juice; soil from low, wet, shady places; soil from a well-cultivated sunny field or garden.

2. Suppose you prepared a solution of sodium hydroxide containing 1 gram-molecular weight of the hydroxide in 1 liter of the solution; also a solution of hydrochloric acid containing 1 gram-molecular weight of hydrogen chloride in 1 liter. How many cubic centimeters of the sodium hydroxide solution would be required to neutralize (*a*) 5 cc. of the hydrochloric acid solution? (*b*) 20 cc.?

CHAPTER XVIII

IONIZATION

Why Solutions conduct the Electrical Current

246. *Introduction.* Some people are content to know merely the facts about things, and others are not satisfied unless they have an explanation of the facts. Many people know that a metal handle on a coffeepot gets too hot for comfort while a wooden one does not; but few inquire why this is so. All practical electricians know that copper is a good conductor of the electric current while sulfur is not, but for the most part they are not inclined to bother about the matter further. We shall not attempt to solve these problems, but a similar question is of great importance to the chemist. Why do some *solutions* conduct the electric current while others do not?

247. Acids, bases, and salts are electrolytes. In the chapter on solutions (§ 119) we learned that pure water does not conduct the electric current (nonelectrolyte), but if we dissolve in the water certain compounds such as sodium chloride or sulfuric acid, the resulting solutions are good conductors (Fig. 116). We gave the name *electrolytes* to those compounds whose solutions conduct the electric current. Moreover, we learned that the passage of a current through a solution of an electrolyte is always accompanied by a chemical change, and that such a change is called *electrolysis.* This general subject becomes of great importance in the study of acids, bases, and salts, for it is a significant fact that *all acids, bases, and salts are electrolytes.* The question naturally arises as to whether the characteristic properties of these compounds may not find some explanation in the very fact that they *are* all electrolytes.

248. Theory of ionization. To explain the facts of electrolysis, as well as many others, the Swedish chemist Arrhenius (Fig. 117) about forty years ago proposed a theory known as the *theory of ionization.* The essential points of the theory, now held to be substantially *facts,* are as follows:

The molecules of all *electrolyies,* when dissolved in water, tend to divide or *ionize* into two electrically charged portions called *ions.* The electrolyte is a polar compound (§ 199, 1), and the one kind of ion has *lost* electrons and is therefore positive (+), while the other kind of ion has *gained* electrons and is negative (–). This exchange of electrons took place when the molecule was formed, and the water merely serves to push apart the oppositely electrified atoms or radicals which have been held together by electrical attraction.

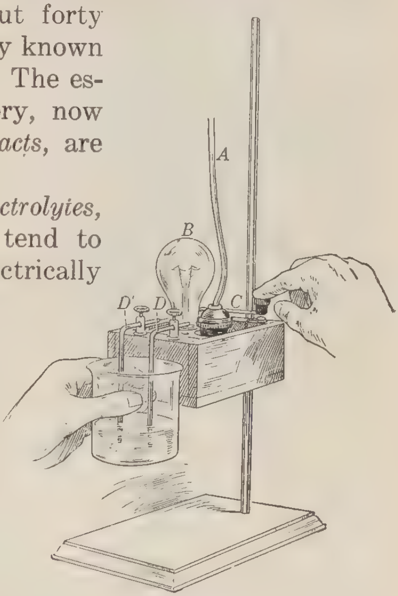


FIG. 116. Testing the conductivity of a solution

The path of the current is through the lamp-cord *A*, the switch *C*, the lamp *B*, through the solution in the beaker from electrode *D* to *D'*, returning to the lamp-cord. If the solution in the beaker is a conductor, the lamp will glow; otherwise it will not glow. The brightness of the lamp indicates the relative conductivity of the solution

With NaCl and H_2SO_4 as examples, ionization may be represented as follows:

$$NaCl \longrightarrow Na^+ + Cl^-$$
$$H_2SO_4 \longrightarrow 2\ H^+ + SO_4^{--}$$

Unless the solution is *very dilute* it does not act as though *all* the electrolyte molecules were ionized. The percentage ionized depends upon a number of factors: (1) *upon the particular electrolyte chosen*; (2) *upon the solvent*, water being the best ionizing solvent; and (3) *upon the amount of solvent present* (the dilution), — the greater the percentage of solvent, the greater is the percentage of electrolyte molecules ionized.

FIG. 117. Svante August Arrhenius (1859–1927)

A Swedish chemist who suggested the theory of ionization

In all such solutions, electrolyte molecules are dividing into pairs of ions, while other pairs of ions are recombining to form molecules, so that a state of equilibrium results. This state is expressed in the equation

$$NaCl \rightleftarrows Na^+ + Cl^-$$

The double arrows indicate that molecules are dividing into ions while at the same time pairs of ions are combining.

Many students find it difficult to understand why the properties of the ions Na^+ and Cl^- are so different from those of the atoms Na and Cl. It must be remembered that the properties of every atom depend upon the number of satellite electrons. The sodium *ion* has lost an electron, while the chlorine *ion* has gained one (§ 199, 1). Consequently the properties of the ions differ from those of the atoms. Many of the "properties" of this world would change if we should lose our moon or gain another.

To be of value, the theory of ionization must give a satisfactory explanation of the properties of solutions. We shall now see whether the theory meets this test.

249. Electrolysis and the theory of ionization. In connection with the preparation of chlorine (§ 211) we saw that it is a *fact* that an electric current in passing through a solution of sodium chloride produces hydrogen, chlorine, and sodium hydroxide. The theory of ionization *accounts* for the formation of these products from the salt as follows: The solution of salt contains the ions Na^+ and Cl^- (Fig. 118). The battery acts very much like an electric pump, pumping some of the electrons belonging to the atoms composing the anode *B* through the connecting wire to the cathode *A*, where they gather in excess. The chlorine ions, each with an extra electron, are attracted to the positively charged anode *B*, to which they give up their extra electrons. They are now atoms of chlorine, and combine to form molecules of chlorine gas. The sodium ions (each deficient in one electron) are attracted to the cathode *A*, recover their lost electrons from the excess supply on the cathode, and become ordinary sodium atoms. These decompose water, yielding hydrogen and sodium hydroxide (§ 211).

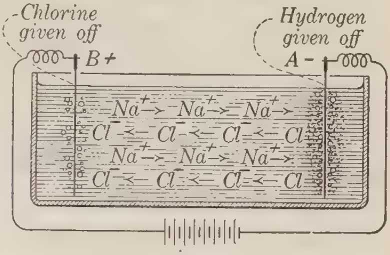


FIG. 118. A diagram illustrating the theory of the electrolysis of a solution of sodium chloride (NaCl)

It is to be carefully noted that the current does not bring about the ionization of the electrolyte, but can pass through the solution only when ions are already present.

250. Acids and the theory of ionization. All acids ionize in solution, forming *positively charged hydrogen ions*, while the remainder of the molecule (usually a radical) forms the negatively charged ion.

$$HCl \longrightarrow H^+ + Cl^-$$
$$H_2SO_4 \longrightarrow 2\,H^+ + SO_4^{--}$$

The hydrogen ion (cation) is common to all acids, while the other ion (anion) varies with the acid. It is therefore reasonable to suppose that the common properties of acids, such as their taste and their action on litmus and metals, must be due to the hydrogen ions. From the standpoint of the theory of ionization *an acid may be defined as a compound which produces hydrogen ions when dissolved in water.*

251. Bases and the theory of ionization. All bases ionize, forming a metal ion (cation) and a hydroxyl ion (anion), thus:

$$NaOH \longrightarrow Na^+ + OH^-$$

The metal ion varies according to the base, but the hydroxyl ion is common to all; hence it is reasonable to conclude that the common properties of bases must be due to the hydroxyl ions. From the standpoint of the theory of ionization *a base may be defined as a compound which produces hydroxyl ions when dissolved in water.*

252. Neutralization and salts and the theory of ionization. Experiments show that hydrogen ions and hydroxyl ions, when brought together, at once unite to form water, a compound which is at most but slightly ionized. If, then, an acid and a base are brought together, the hydrogen ions of the acid and the hydroxyl ions of the base unite, thus:

$$H^+, Cl^- + Na^+, OH^- \longrightarrow Na^+, Cl^- + H_2O$$

The Na^+ of the base and the Cl^- of the acid are thus the only ions left in solution, and are the ions of the salt NaCl. From the standpoint of the ionization theory, therefore, the terms *neutralization* and *salt* may be defined as follows:

Neutralization consists in the union of equal numbers of the hydrogen ions of an acid and the hydroxyl ions of a base to form water.

A salt is a compound formed by the union of the negatively charged ion of an acid with the positively charged ion of a base.

253. Strength of acids and bases. Since acid and basic properties are due to hydrogen ions and hydroxyl ions, that acid or base which will produce the greatest percentage of these ions at a given concentration must be regarded as the strongest representative of its class. The acids and bases described in the foregoing paragraphs are all quite strong. In 10 per cent solutions about half of the molecules are dissociated into ions, and this is also approximately the extent to which most salts are ionized at this same concentration.

254. Ionization and the electrolysis of water. The reason for adding sulfuric acid to water in the preparation of oxygen and hydrogen by electrolysis is readily explained by the theory. Pure water is very little ionized, and so cannot conduct an electric current. Sulfuric acid is an electrolyte, and when dissolved in water it ionizes to give the ions $2\,H^+$ and SO_4^{--}. During the electrolysis of the solution, the H^+ ions travel to the cathode (negative), recover their lost electrons from it, and, as hydrogen atoms, combine to form molecules of hydrogen gas. The SO_4^{--} ions move to the anode (positive), surrender their excessive electrons to it, and the uncharged group SO_4 then acts upon water, setting free oxygen, thus:

$$2\,SO_4 + 2\,H_2O \longrightarrow 2\,H_2SO_4 + O_2$$

The sulfuric acid so formed now ionizes, and the process continues as long as any water is left. The hydrogen and oxygen evolved thus come either directly or indirectly from the water, and in the proportion in which they are present in it.

255. Methods of expressing reactions between compounds in solution. Chemical equations representing reactions between substances in solution may represent the details of the reaction, or they may simply indicate the reacting substances and the final products formed. Thus, if we wish to call attention to the details of the reaction between sodium hydroxide and hydrochloric acid in solution, representing the ions which take part in the reaction, we write the equation as follows:

$$Na^+, OH^- + H^+, Cl^- \longrightarrow Na^+, Cl^- + H_2O$$

If, on the other hand, we wish simply to represent substances taking part in the reaction and the final products formed, we write the equation thus:

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

256. Electrochemical (or displacement) series. When a piece of zinc is put into an acid, zinc passes into solution and hydrogen is evolved:

$$Zn + 2\ HCl \longrightarrow ZnCl_2 + H_2$$

or $$Zn + 2(H^+, Cl^-) \longrightarrow Zn^{++}, Cl^-Cl^- + H_2$$

In like manner, when zinc is placed in a solution of a salt of copper, such as the sulfate $CuSO_4$, zinc passes into solution, and a corresponding quantity of copper is precipitated:

$$Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$$

or $$Zn + Cu^{++}, SO_4^{--} \longrightarrow Zn^{++}, SO_4^{--} + Cu$$

It will be seen that the anions Cl^- and SO_4^{--} take no part in the reaction, since they appear on both sides of the equation. The important fact in the reaction is that in each case the zinc atoms give up two electrons, in the first case to hydrogen ions and in the second case to copper ions; so the equations might be written

$$Zn + 2\ H^+ \longrightarrow Zn^{++} + H_2$$

and $$Zn + Cu^{++} \longrightarrow Zn^{++} + Cu$$

Copper ions and hydrogen ions can both recover their lost electrons from zinc atoms. On the other hand, copper has no effect upon a solution of zinc sulfate.

It has been found to be possible to arrange hydrogen and the metals in a table in such a way that any element in the list will displace any one *below* it from its salts and will in turn be displaced from its salts by any one *above* it. This list is called the *electrochemical series* (or the *displacement series*).

ELECTROCHEMICAL SERIES

1. Lithium
2. Potassium
3. Sodium
4. Calcium
5. Magnesium
6. Aluminum
7. Manganese
8. Zinc
9. Chromium
10. Iron
11. Cadmium
12. Cobalt
13. Nickel
14. Lead
15. Tin
16. **Hydrogen**
17. Copper
18. Antimony
19. Bismuth
20. Arsenic
21. Mercury
22. Silver
23. Platinum
24. Gold

This table enables us to foretell many reactions. For example, from the positions of the two metals we should expect magnesium to displace tin from its salts, and so it does:

$$Mg + SnCl_2 \longrightarrow MgCl_2 + Sn$$

We should not, however, expect iron to displace aluminum.

It is of especial interest to notice the position of hydrogen in the series. All the metals above it will evolve hydrogen from acids, while those below it will not. In the latter case, if any action takes place it is preceded by oxidation.

It will be recalled that sodium liberates hydrogen from water as well as from acids. All the metals above hydrogen do this, though in many cases the action is very slow.

257. The value of a theory once more. The theory of ionization gives us a plausible and in general a very satisfactory explanation of a large number of apparently unrelated facts — the electrolysis of salt and of water; the nature of acids, bases, salts, and neutralization; the differing strengths of acids and bases; the replacement of metals by each other. Without this theory we have no good explanation of any one of these things. Although there is uncertainty about some of the details of the theory, chemists feel that in the main it is a picture of the truth.

258. Formation of crystals from solution. If salts in solution are in the form of ions as well as molecules, it is of interest to know whether a crystal growing in a solution is being formed from the separate ions or from the molecules. By X-ray photographs it has been possible to prove that the crystal consists of separate atoms or ions, arranged alternately in regular rows in three space-directions and spaced apart evenly throughout the crystal (Fig. 119). Molecules as such are not present in crystals, but in a sense each crystal is one gigantic molecule, and it is most likely that the crystal grows by the addition of ions rather than molecules.

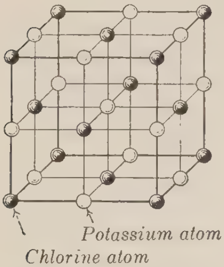


FIG. 119. Drawing illustrating the arrangement of the atoms in a crystal of potassium chloride

From what has been said it will not be surprising to learn that when we melt an electrolyte, and so destroy its crystal structure, the resulting liquid is a good conductor and highly ionized. Many metals can be prepared by electrolysis of their fused salts. It will also be clear why we cannot determine the molecular weight of a solid (§ 131).

CHAPTER SUMMARY IN QUESTION FORM

1. What name is given to a compound whose solution in water (*a*) conducts the electric current? (*b*) does not conduct the electric current?

2. Give an example of a liquid that is (*a*) a conductor; (*b*) a nonconductor.

3. Is the passage of a current through a liquid accompanied by (*a*) a physical change or (*b*) a chemical change or (*c*) neither?

4. What is meant by the word *electrolysis*?

5. What groups of compounds are all electrolytes?

6. (*a*) Who formed a theory to account for the facts of electrolysis? (*b*) What is the theory called?

7. Give the essential parts of the theory of ionization, and illustrate by reference to what happens when sodium chloride is dissolved in water.

8. Write an equation which expresses the fact that in a solution of sodium chloride a state of equilibrium exists between the molecules of sodium chloride and the ions formed from the molecules.

9. By the use of the equation in question 8, how could we overcome the equilibrium (*a*) so as to increase the number of molecules of sodium chloride present? (*b*) so as to increase the number of ions present?

10. From the list given below select the word or phrase to which each of the following descriptions applies: (*a*) found in all acids; (*b*) found in all bases; (*c*) the positive part of an ionized compound; (*d*) the negative part of an ionized compound; (*e*) contains hydrogen ions; (*f*) contains anions from the acid and cations from the bases; (*g*) consists in the union of the hydrogen ions of the acid and the hydroxyl ions of the base; (*h*) the electrode where there is an excess of electrons; (*i*) the electrode where there is a deficiency of electrons.

Cathode
Ions
Anion
Cation
Hydrogen ions
Hydroxyl ions
Acid
Base
Salt
Neutralization
Anode

11. Some sodium chloride is dissolved in water and a current of electricity is passed through the solution. Does the sodium chloride ionize as it dissolves, or not until the current is passed through the solution?

12. Explain what is meant by the following words or phrases, in terms of the theory of ionization: (*a*) acid; (*b*) base; (*c*) salt; (*d*) neutralization; (*e*) strong acid; (*f*) weak base.

13. Show how the theory of ionization accounts for the fact that pure hydrogen chloride will not change blue litmus red, but its solution in water will produce this change.

14. (*a*) What are the products formed when a current of electricity is passed through a solution of sodium chloride? (*b*) Show how the theory of ionization accounts for the formation of these products.

15. Write an equation expressing the reaction between hydrochloric acid and sodium hydroxide in solution, to represent (*a*) the details of the reaction (ionic equation); (*b*) the final products only.

16. What name is given to the grouping of hydrogen and the metals in such a way that any element in the list will replace any one below it from solutions of its salts?

THOUGHT QUESTIONS

1. If sodium chloride ionizes in solution, why do we get no evidence of the presence of sodium or of chlorine in the solution?

2. Will any compound show acid properties except in the presence of water?

3. Account for the presence of sodium hydroxide in a solution of sodium chloride through which a current of electricity is passing.

4. From the standpoint of the theory of ionization, write the equations for the following reactions: (*a*) nitric acid and sodium hydroxide; (*b*) sulfuric acid and sodium hydroxide; (*c*) hydrochloric acid and calcium hydroxide.

5. Predict what would happen if a strip of copper were placed in a solution (*a*) of silver nitrate; (*b*) of zinc sulfate; if a strip of zinc were placed in a solution (*c*) of silver nitrate; (*d*) of copper sulfate.

6. In general, would you expect a metal that liberated hydrogen from water to liberate hydrogen from acids also?

7. Where in the electrochemical series would you expect to find those elements that are found free in nature?

FOR HONOR STUDENTS

1. Write a theme on "The Value of Theories," illustrating your statements by reference to the theory of ionization.

2. From the standpoint of the theory of ionization, predict what would happen if you passed a current of electricity through (*a*) a solution of copper sulfate; (*b*) a solution of sodium sulfate.

CHAPTER XIX

NITROGEN AND SOME RARE GASES

Gases that act with Difficulty or Not at All

259. ***Introduction.*** We have seen that it is the oxygen of the air that supports life, and that it is a very active element. The activity of atmospheric oxygen is held in check by a large percentage of the gaseous element nitrogen, which will neither burn nor support combustion. Nitrogen is accompanied in minute percentages by a number of still less active gases that will not combine with anything. All these inactive gases are of interest.

Nitrogen

260. **General.** In every 100 volumes of *dry* air there are about 78 volumes of free nitrogen. This means that we live at the bottom of an enormous sea of this gas. Combined with other elements, nitrogen occurs in our foods and in our bodies, being essential to our lives and to the lives of all animals and plants. It also occurs in certain places as potassium nitrate (KNO_3), often called *saltpeter*; and as sodium nitrate ($NaNO_3$), sometimes called *Chile saltpeter.*

261. **Physical properties.** Like oxygen and hydrogen, nitrogen is a colorless gas without odor or taste and but slightly soluble in water. At very low temperatures and under great pressure it condenses to a colorless liquid which boils at $-195.8°$. At still lower temperatures it is obtained in the form of a white solid, resembling ice in appearance, which melts at $-209.8°$.

262. Preparation. On a large scale nitrogen is always prepared from liquid air, as will be described in the following chapter. In the laboratory it is prepared by one of the following methods:

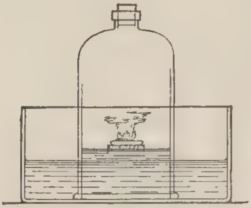


FIG. 120. Preparation of nitrogen

Phosphorus combines with the oxygen of the air to form a soluble solid, leaving the nitrogen

1. ***Preparation from air.*** Oxygen is very much more active than nitrogen; so that it is possible to obtain the nitrogen by passing air over some substance that will combine with the oxygen only, leaving the nitrogen unchanged. Such a substance must be chosen to combine with the oxygen as will form a product that is either a liquid or a solid, so that it can be separated easily from the nitrogen gas. Phosphorus is sometimes used for this purpose (Fig. 120), since it has a strong affinity for oxygen, but the process requires great care. More often copper is used. When air is passed through a tube filled with hot copper gauze the oxygen in the air combines with the copper to form a black solid, copper oxide (CuO), which remains in the tube, while the nitrogen passes on and is collected (Fig. 121).

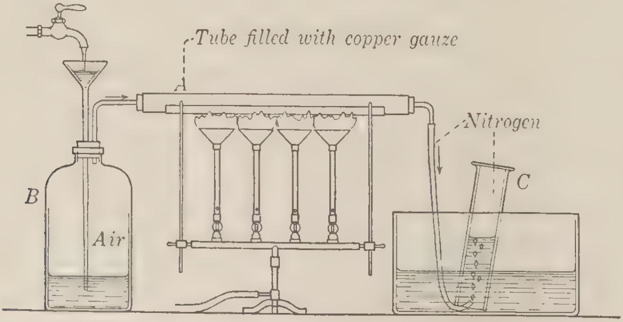


FIG. 121. Preparing nitrogen from air with hot copper

Air from the bottle B is forced over hot copper in the tube A by pouring water into the funnel. The copper removes the oxygen, and the nitrogen collects in C

2. ***Preparation from compounds of nitrogen.*** Nitrogen obtained from air is never entirely pure, since it contains small percentages of the rare elements helium, argon, neon, krypton, and xenon, originally present in the air. These rare elements constitute only about 1 per cent of the nitrogen, and, since they resemble nitrogen in most respects, do not materially affect its properties. Perfectly pure nitrogen may be obtained by decomposing some of its compounds. The one known as ammonium nitrite (NH_4NO_2) is the one generally used. When this is heated it decomposes into water and nitrogen:

$$NH_4NO_2 \longrightarrow 2\,H_2O + N_2$$

263. Chemical conduct. At ordinary temperatures nitrogen is very inactive. It does not easily combine with oxygen even at the temperature of a hot fire, as is evident from the fact that air contains such large quantities of both these gases in a free state; nor does it combine with any other elements very readily, as is apparent from the fact that there is so much of it in the air and so little in the earth's crust in combination with other elements.

At extremely high temperatures nitrogen is much more active. Under proper conditions it will then combine with oxygen to form an oxide of nitrogen (NO), and with hydrogen to form ammonia (NH_3) — a gaseous compound whose solution in water we may buy under the name *aqua ammonia* or *ammonia water*. At high temperatures nitrogen also combines with many of the metals. The resulting compounds are called *nitrides* just as compounds of an element with oxygen are called *oxides*.

264. Uses of nitrogen. The chief use of nitrogen in industry is in the preparation of ammonia (NH_3), which is the first step in the manufacture of important fertilizers. Smaller amounts are used in the manufacture of calcium cyanamide, which is also used as a fertilizer. Some electric-light bulbs are filled with the gas.

265. The fixation of nitrogen by plants. Nitrogen is a necessary part of all living things, both plant and animal. Yet few of them can take free nitrogen from the air and build it into living matter. They must get their nitrogen food from *compounds* of nitrogen, and these are not abundant either in the air or in the soil. Where does the supply come from?

Farmers have long known that crops of clover, peas, beans, and similar plants improve the soil, and more recently scientific men have shown *why* this is so. On the roots of these plants are little *nodules* that look like minute potatoes on the roots of a potato plant (Fig. 122). In reality these are the homes of myriads of bacteria that in some way bring about the combination of free nitrogen from the air with other elements (chiefly oxygen), and the compounds so formed dissolve and provide food for plants. This process of causing free nitrogen to combine with other elements is called *fixation of nitrogen* — in this case brought about by the so-called nitrifying bacteria.

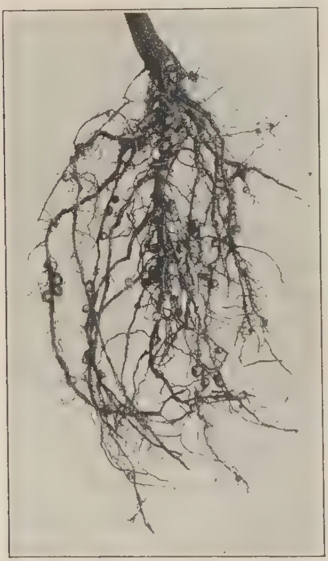


FIG. 122. Nodules on the roots of a soy-bean plant

The "Lazy" Elements of the Atmosphere

266. General. For centuries chemists have studied the atmosphere, and they thought they knew its composition accurately. Great was their surprise when the English chemist Ramsay (Fig. 123) and his associates, about thirty years ago, discovered five new gaseous elements to be

FIG. 123. Sir William Ramsay (1852–1916)

An English chemist, who, together with the English scientist Lord Rayleigh, discovered argon. In association with Travers he also discovered the elements xenon, neon, and krypton and was the first to show that helium exists on the earth. For these and other outstanding discoveries, Ramsay was awarded the Nobel prize in 1904

FIG. 124. Robert Wilhelm Bunsen (1811–1899)

A distinguished German chemist. Bunsen discovered rubidium and cesium by means of the spectroscope, — an instrument devised by Bunsen and Kirchhoff. He also devised a filter pump, a galvanic cell, a laboratory gas burner (Bunsen burner), and other useful apparatus. He worked out a method for preparing magnesium on a large scale and contributed much to our methods for analyzing gases

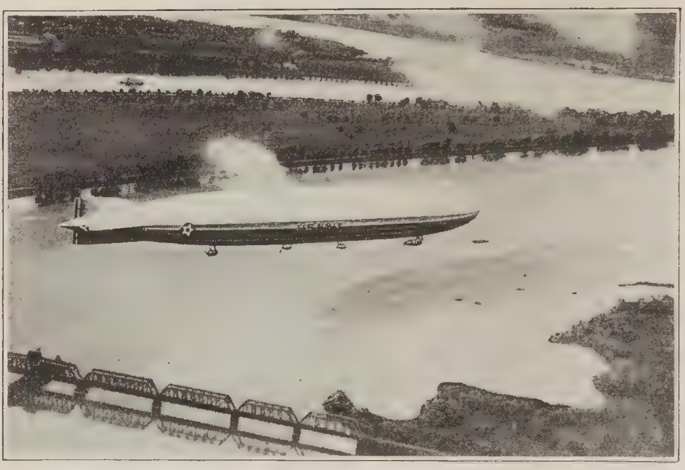


FIG. 125. View of the first helium-filled dirigible in its flight over the Potomac River at Washington, D.C., December, 1921

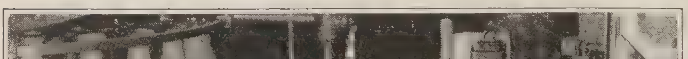


FIG. 126. Filling electric-light bulbs with argon

present in the atmosphere in minute percentages. These elements are helium, neon, argon, krypton, and xenon. They are all colorless, odorless gases, and are very strange elements because *they do not combine with any other elements* and form no compounds. It is because of this fact that we sometimes call them the "lazy" elements.

267. Helium. It is a very interesting fact that helium was known to exist on the sun long before anyone was able to detect it on the earth. Its presence on the sun was detected by means of the spectroscope (§ 269), an instrument which enables us to tell just what elements are present in any light-giving body. So far as we know, the American chemist Hillebrand was the first who actually obtained helium, although he did not know that he had it. He found that when certain rare minerals are heated a gas is given off. He tested this gas and concluded that it was nitrogen. A few years later the English chemist Ramsay repeated Hillebrand's experiments, and found that the gas evolved on heating the minerals was chiefly helium. There is no doubt, therefore, that Hillebrand had obtained helium, although he failed to recognize it.

There is very little helium in the atmosphere — about 4 volumes in 1,000,000. Small percentages are present in the natural gas of certain localities, and this is the only practical source of helium. Next to hydrogen it is the lightest of all gases, being about twice as heavy as hydrogen. It is prepared in considerable quantities in the United States, especially from the gas wells of Texas and Utah, and is used for inflating balloons and dirigibles (Fig. 125); although it has $7\frac{1}{2}$ per cent less lifting power than hydrogen, this disadvantage is more than offset by the fact that it will not burn and so is safer than hydrogen, which is so very inflammable.

One other property of helium should be mentioned: *it is the most difficult of all gases to liquefy.* Liquid helium boils at $-268.9°$; solid helium melts at $-272.2°$. The latter approaches *absolute zero* (−273°) — a temperature which is believed to mark the entire absence of heat.

268. Neon, argon, krypton, and xenon. With the exception of helium, which is obtained from natural gas, the remaining members of the group of "lazy" elements are all obtained from liquid air, as will be described in the following chapter. Neon is coming into use very largely in the red-glowing "neon signs," which consist of glass tubes containing a small amount of neon through which a current of electricity is passed. Many of the electric-light bulbs are now filled with argon (Fig. 126), so that this gas also is used in considerable amounts. Krypton and xenon have as yet no commercial uses.

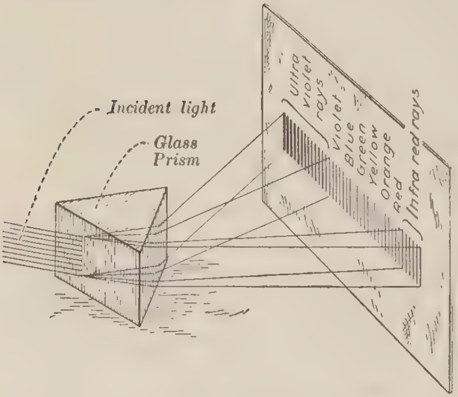
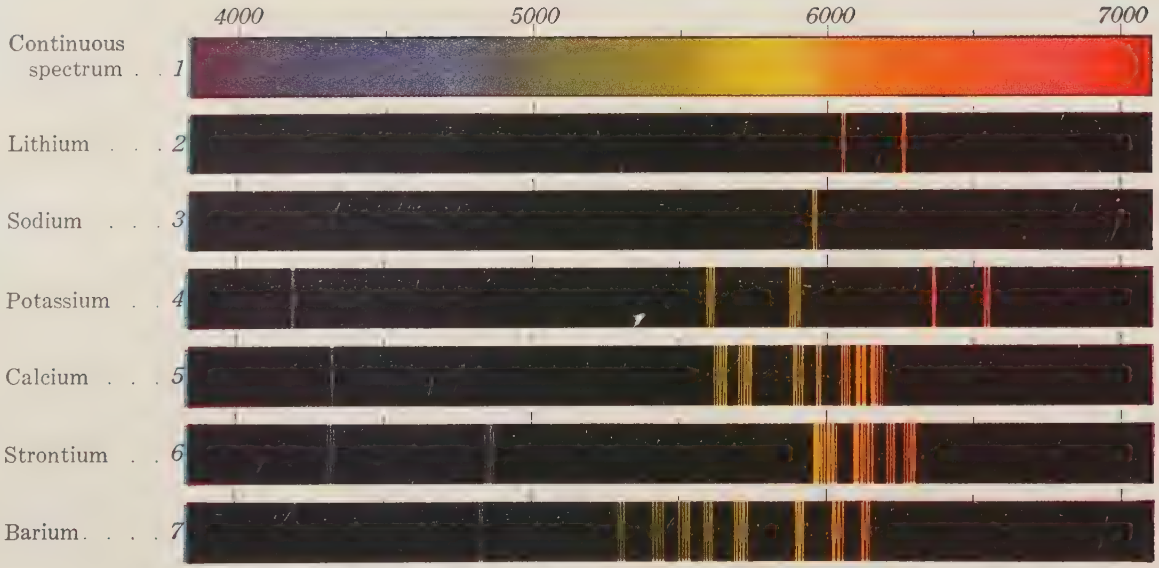


FIG. 127. Diagram showing how a beam of white light is separated into its constituents

269. The spectroscope. As we have stated, the discovery of helium was made by use of the spectroscope. A number of other elements as well have been discovered in this way, so that the instrument is of great value. It is important that we should know at least the principle involved in its construction and use.

When a beam of light passes through a triangular prism of glass, it is bent out of its course and emerges at a decided angle with its original direction, as is shown in Fig. 127. Ordinary light is made up of waves of many different wavelengths, and each one is bent, or *refracted*, to a different degree, so that the various colors of which the light is composed are spread out in a band of colors known as



A CONTINUOUS SPECTRUM AND SIX BRIGHT-LINE SPECTRA

These seven colored bands are typical of the many that may be seen in the spectroscope. Number 1, called a *continuous* spectrum, is an unbroken gradation of colors ranging from violet to red, and is seen when a spectroscope is directed at a solid body heated to incandescence. The others are *bright-line* spectra and are examples of what is seen in the spectroscope when various elements (or their compounds) are vaporized in a Bunsen flame or in an electric arc, each spectrum being characteristic of some one element. The numbers at the top refer to the wave lengths of the light, measured in suitable units a spectrum, the red being the least refracted, the violet the most so. A beam of *white* light gives a continuous band of colors, from red through orange, yellow, green blue, to violet, called a *continuous spectrum* (see illustration opposite this page). The spectrum of any *colored* light is not continuous, but shows merely lines of those colors of which the light is composed.

Now the light emitted by the glowing vapor of any element gives a definite spectrum, and no two elements have the same spectrum. If we know the spectra of all the elements, then we can find out just what elements are present in any light-emitting substance by examining the spectrum of the substance. A new spectrum would then mean that a new element must be present. In this way helium and a number of other elements were discovered.

CHAPTER SUMMARY IN QUESTION FORM

1. Where does nitrogen occur (*a*) in the free state? air (*b*) in the combined state? in [illegible]

2. Give three physical properties that nitrogen has in common with hydrogen and oxygen. [illegible]

3. Suppose you were given three bottles filled with hydrogen, oxygen, and nitrogen respectively. How could you recognize each?

4. What property of oxygen makes it possible to remove the oxygen from a mixture of oxygen and nitrogen?

5. Explain what happens when a current of air is passed over hot copper.

6. Name three elements with which nitrogen will combine directly.

7. Give two important uses of nitrogen in industry.

8. Plants such as clover, peas, beans, and alfalfa have the power of taking nitrogen from the air and converting it into compounds of nitrogen. (*a*) What is this process called? (*b*) By what agencies is it brought about? (*c*) Of what value is this process to all of us?

9. (*a*) Name the "lazy" elements. (*b*) Name the discoverer of each. (*c*) Which ones have uses in industry, and for what purposes?

10. What property of the "lazy" elements distinguishes them from all other elements? [illegible]

11. A beam of white light is passed through a triangular glass prism; also a beam of colored light. State the result in each case.

12. (*a*) What instrument is used for obtaining the spectrum of an element? (*b*) How has it enabled chemists to discover new elements? (*c*) Name one element discovered in this way.

THOUGHT QUESTIONS

1. In preparing nitrogen from the air, why not use carbon or sulfur for removing the oxygen?

2. Viewed from the standpoint of the structure of the atom, should you expect nitrogen to combine readily with oxygen?

3. Give two reasons why the "lazy" elements remained so long undiscovered.

4. Account for the fact that the "lazy" elements do not form compounds.

5. (*a*) What is the great objection to the use of hydrogen for inflating airships? (*b*) Why not use nitrogen for the purpose?

6. Mention different ways in which a farmer enriches the soil.

7. Suppose you passed 100 liters of dry air through a tube containing hot copper. (*a*) What volume of nitrogen would you obtain? (*b*) What product would be left in the tube? (*c*) How much more than the original copper would this product weigh?

8. A candle flame is extinguished when placed in nitrogen, yet many electric-light bulbs are filled with pure nitrogen. Explain.

FOR HONOR STUDENTS

1. (*a*) Make a list of the elements so far studied. (*b*) Find in your dictionary the derivation of each name. (*c*) Do you think the name of each has been appropriately chosen?

2. Write a theme on the spectroscope, pointing out some of the discoveries made through its use. (Consult encyclopedia.)

CHAPTER XX

THE ATMOSPHERE

An Ocean of Gas surrounding the Earth

270. ***Introduction.*** We are all familiar with the ocean of water that covers a large part of the earth's surface, sometimes reaching a depth of six or seven miles. Many of us, however, do not stop to realize that the entire earth is covered with a much deeper ocean of gases, which we term the *atmosphere.* The mixture of gases which compose the atmosphere extends many miles in height — certainly more than a hundred miles. It is densest at the earth's surface, and gradually fades away as the distance from the earth increases; so mountain-climbers and aviators must take with them a supply of oxygen if they ascend more than four or five miles above the earth.

The mixed gaseous material of which the atmosphere is made up is called *air.* Inasmuch as air is composed principally of a mixture of oxygen and nitrogen, elements which have already been described, its properties may be inferred largely from those of the two gases.

/ 271. **Composition of the air.** The normal constituents of air, together with the approximate volumes of each in samples collected in the open fields, are as follows:

Oxygen	21 volumes in 100 volumes of dry air
Nitrogen	78 volumes in 100 volumes of dry air
Water vapor	variable within wide limits
Argon	94 volumes in 10,000 volumes of dry air
Carbon dioxide	3 to 4 volumes in 10,000 volumes of dry air
Hydrogen, helium, neon, krypton, xenon, ozone	traces

In addition, most air, especially in thickly populated districts, contains dust particles, bacteria, and certain gases evolved in manufacturing processes.

272. Water vapor in the air. The quantity of water vapor which may be present in the air varies with the temperature. This is shown in the following table, which gives the weight in grams of the water vapor that 1 cubic meter of air can absorb at the temperature indicated:

Temperature	0°	10°	20°	30°
Weight of water . .	4.8 g.	9.9 g.	17.1 g.	30 g.

273. Constituents of the air that are essential to life. The constituents that are known to be essential to life are oxygen, nitrogen, water vapor, and carbon dioxide. The oxygen in the atmosphere directly supports life through the process of respiration. The nitrogen serves to dilute the oxygen and thus to diminish the intensity of its action. The water vapor prevents too much evaporation of the water present in living things. The carbon dioxide is an essential plant food.

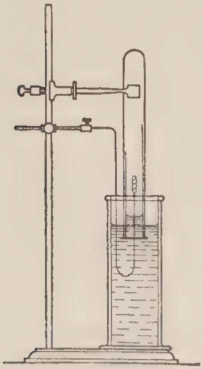


FIG. 128. Phosphorus (on the end of the wire) removes the oxygen from air and leaves the nitrogen

274. The analysis of air. The question arises, How can we measure the percentage of each of the constituents present in the air? A number of methods are known for measuring the different constituents, among which are the following:

1. ***Oxygen.*** A measured volume of air (from which carbon dioxide and water vapor have been removed) is acted on by phosphorus or hot copper, which removes all the oxygen. The decrease in the volume of air gives us the volume of oxygen withdrawn (Fig. 128).

2. ***Nitrogen.*** The gas remaining after the removal of the oxygen is passed over hot magnesium, which combines with the nitrogen. The decrease in volume is again noted; this equals the volume of nitrogen removed. The small amount of gas remaining is composed of argon and the other rare elements present in air.

3. ***Water vapor and carbon dioxide.*** These two constituents are determined by passing a known volume of air through two tubes, the first filled with calcium chloride, and the second with sodium hydroxide. The calcium chloride removes the water vapor, and the sodium hydroxide removes the carbon dioxide. The tubes and contents are weighed before and after the air is passed through them. The increase in their weights gives us the weights of water vapor and carbon dioxide respectively in the original volume of air.

275. Processes tending to change the composition of the air. There are a number of processes taking place about us that tend to increase the carbon dioxide in the air, while others tend to diminish it.

1. ***Processes tending to increase the quantity of carbon dioxide.*** Not only do large quantities of carbon dioxide escape into the atmosphere from volcanoes and crevices in the earth's crust, but certain more widespread processes give off this gas. Chief among these are the following:

(a) *Respiration.* In respiration some of the oxygen in the inhaled air is absorbed by the blood and carried to all parts of the body, where it combines with the carbon of the worn-out tissues and with that of fuel material supplied by digestion. The products of oxidation are carried back to the lungs and exhaled largely in the form of carbon dioxide.

(b) *Combustion.* All the ordinary fuels contain large percentages of carbon. On burning, this is oxidized to carbon dioxide.

(c) *Decay of organic matter.* When organic matter decays in the air much of its carbon is oxidized to carbon dioxide.

2. ***Processes tending to decrease the quantity of carbon dioxide.*** There are two general processes which tend to diminish the quantity of carbon dioxide in the atmosphere:

(a) *The growth of plants.* When growing in sunlight, plants absorb carbon dioxide from the air, retaining the carbon, and returning a portion of the oxygen to the air. It is from this source that plants obtain their entire supply of carbon.

(b) *The weathering of rocks.* Large quantities of carbon dioxide are constantly being withdrawn from the atmosphere through its combination with various rock materials.

These opposite changes are represented in Fig. 129.

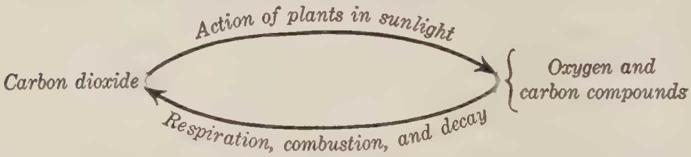

Action of plants in sunlight
Carbon dioxide
Oxygen and carbon compounds
Respiration, combustion, and decay

FIG. 129. Production and removal of atmospheric carbon dioxide

276. Composition of the air nearly constant. While a number of changes are taking place which tend to alter the composition of the air, nevertheless the results of a great many analyses of dry air collected from year to year in the open fields show that the percentages of oxygen, nitrogen, and carbon dioxide are very nearly constant. How do we account for this constant composition? The answer is as follows: (1) The changes caused by the processes of combustion, respiration, and decay on the one hand, and the growth of plants and the weathering of rocks on the other, tend to balance each other and come to an equilibrium. (2) The volume of the air is so vast, and the changes that occur so small in comparison with the total volume of air, that they are difficult to detect, especially since the winds keep the air in motion and so prevent marked local changes.

277. Are the oxygen and nitrogen in the air combined or simply mixed together? We have seen that the percentages of nitrogen and oxygen in the air are nearly constant. Now constancy of composition is characteristic of chemical compounds. The question may then be asked, Is not the air a compound of nitrogen and oxygen rather than a mixture of these gases? That they are not combined may be proved in a number of ways, among which are the following:

1. While the percentages of oxygen and nitrogen are nearly constant, they are not so constant as they would be were the two elements combined in the form of a compound.
2. When liquid air boils, the nitrogen passes off first; were the nitrogen and oxygen combined, they would pass off together, just as the hydrogen and oxygen in water pass off together when water is boiled.

278. Impure air and ventilation. The difference in the percentages of oxygen, carbon dioxide, and moisture present in inhaled and exhaled air is shown in the following table:

CONSTITUENT	INHALED AIR	EXHALED AIR
Oxygen	21.00%	16.00%
Carbon dioxide	0.04%	4.38%
Water vapor	Variable	Saturated

The injurious effects resulting from inadequate ventilation seem to be due neither to lack of oxygen nor to the excess of carbon dioxide; rather they are due to high temperature and to the presence of an abnormal amount of water vapor, both of which conditions are apt to prevail in crowded and poorly ventilated rooms. In general, a moisture content of about 70 per cent of that required for saturation is most conducive to comfort. The volume of fresh air necessary for good ventilation varies greatly with conditions, but it may be said to be about 30 cu. ft. per minute for each person present.

279. Liquid air. We have learned that all gases, if cooled and compressed sufficiently, may be changed into liquids or even solids. Some gases, such as sulfur dioxide

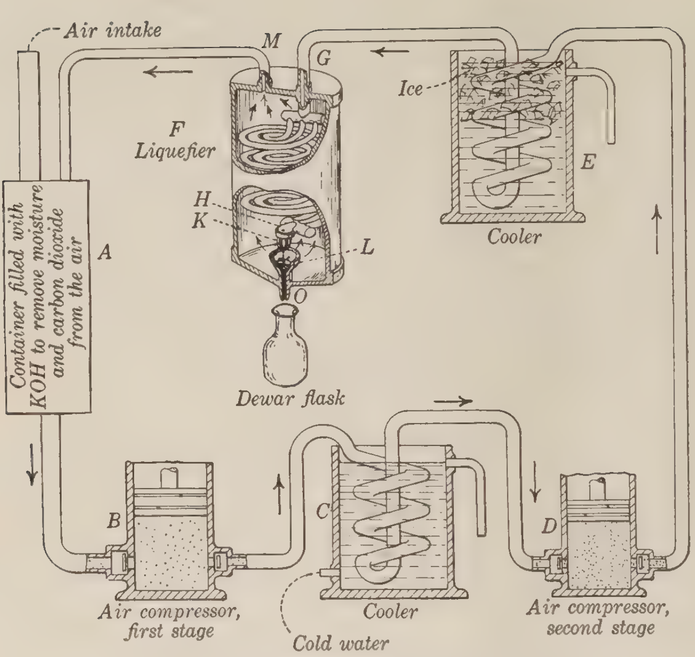

Air intake
M
G
F
Liquefier
Ice
E
H
K
L
Cooler
A
Container filled with KOH to remove moisture and carbon dioxide from the air
O
Dewar flask
B
C
D
Air compressor, first stage
Cooler
Cold water
Air compressor, second stage

FIG. 130. The steps in the liquefaction of air

The air enters the apparatus at the air intake and passes through the chamber *A* filled with absorbents for moisture and carbon dioxide. It then enters the air compressor *B*, where it is highly compressed. Heat is evolved in this process, and the compressed hot air is cooled by cold water in the cooler *C*. It undergoes further compression in *D* and is again cooled in *E*. The highly compressed cold air then enters the liquefier *F*. Inside the liquefier the conducting tube *G* divides into three smaller copper tubes (to increase the surface) wound into a spiral, and these unite at *H* into a single large tube. There is a very small opening at *K*, through which some of the compressed air escapes and expands to atmospheric pressure. In expanding it becomes very cold, and is led back over the copper tubes to cool the air within them. As the process continues, the air in the tubes becomes increasingly cold until it reaches the temperature of liquefaction, when drops of liquid air form and collect in the cup *L*, from which it is drawn off into the Dewar flask at *O*

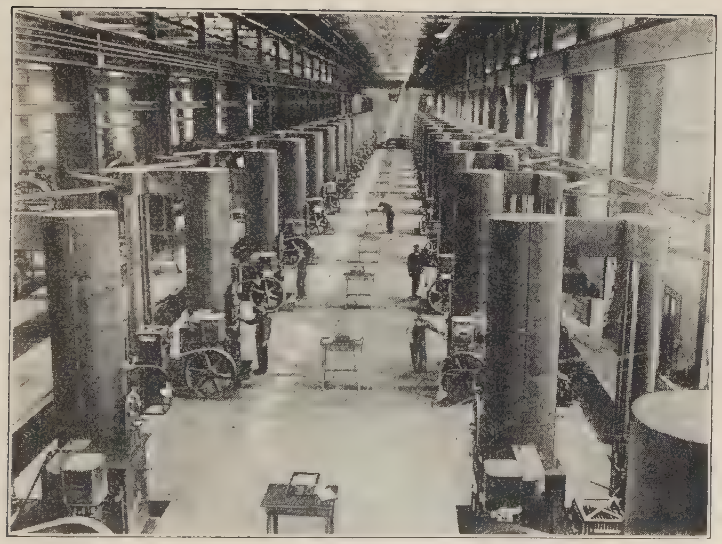


FIG. 131. A liquid-air plant in operation

Fig. 130 shows the different steps required in liquefying air, while Fig. 131 gives a view of a liquid-air plant in actual operation. The plant shown is one built during the World War at Muscle Shoals, Alabama. The engines used in compressing the air appear on the extreme left of the figure. The compressed air is first cooled by water and then still further cooled by being made to run small engines, one of which is shown at the base of each of the large columns. In this process energy of heat is changed into energy of motion, which results in the cooling of the compressed air to a temperature at which it liquefies as it passes through the liquefier (see Fig. 130). In the Muscle Shoals plant the liquid air is used for the preparation of nitrogen. To separate the nitrogen from the oxygen, the liquid air is forced into the top of the large columns shown in the figure. As it flows down the metal plates on the inside of the columns, the nitrogen present separates (boils) in gaseous form, since it boils more readily than the oxygen. This process serves for the commercial preparation of both nitrogen and oxygen. In the Muscle Shoals plant three hundred tons of nitrogen can be obtained each twenty-four hours (the gas formed when sulfur burns in air) (§ 47), are easily condensed; others, such as oxygen and nitrogen, with more difficulty; while helium is the most difficult of all to condense (§ 267), its liquefaction by the Dutch physicist Kamerlingh Onnes in 1908 being regarded as one of the great achievements of science.

Air was first obtained in the liquid state about fifty years ago. The method used has been improved (Figs. 130, 131) until now liquid air is an article of commerce. It is essentially a mixture of liquid nitrogen (boiling point, – 195.8°) and liquid oxygen (boiling point, –183°). Advantage is taken of this difference in the boiling points of oxygen and nitrogen to separate these two gases from each other in the commercial process for obtaining oxygen and nitrogen on a large scale. From the same source and by the same method neon and argon are obtained. The extremely low temperature of liquid air may be inferred from the fact that when immersed in it mercury is frozen to a mass so hard that it may be used as a hammer head for driving nails.

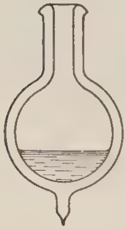


FIG. 132. A Dewar flask used for holding liquid air

280. Dewar flasks; thermos bottles. Liquid air may be kept for some hours in a special form of flask devised by the Scottish scientist Dewar, known as a *Dewar flask*. This consists of two concentric vessels (Fig. 132) of any convenient shape. These are joined together at the upper rim only, and the space between them is exhausted by an air pump. The vacuum serves as the best possible insulator to prevent conduction of heat. The surface of the outer flask is often silvered in order to reflect the external heat and

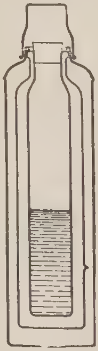


FIG. 133. A thermos bottle

thus prevent its absorption. *Thermos bottles* (Fig. 133) are constructed on the same plan and are very effective for keeping liquids either hot or cold for several hours.

CHAPTER SUMMARY IN QUESTION FORM

1. (*a*) Name five gases present in appreciable percentages in the air. (*b*) Give the volumes of each of the gases present in 100 volumes of dry air.

2. Name five gases, mere traces of which are found in the air.

3. (*a*) Name four constituents of the air that are necessary to life. (*b*) Give the part each of these plays in supporting life.

4. How can you determine the percentage (*a*) of oxygen in the air? (*b*) of nitrogen? (*c*) of carbon dioxide? (*d*) of water vapor?

5. Name (*a*) three processes that occur in nature that tend to increase, and (*b*) two processes that tend to decrease, the quantity of carbon dioxide in the air.

6. Do the results of many analyses of the air collected in the open fields show that the percentages of oxygen, nitrogen, and carbon dioxide (*a*) are constant? (*b*) are very nearly constant? (*c*) vary through a wide range? (*d*) gradually change as the years pass?

7. (*a*) Are the nitrogen and oxygen in the air combined or simply mixed together? (*b*) Give two reasons in support of your answer.

8. Which of the following statements is correct: (*a*) air is a compound; (*b*) air is an element; (*c*) air is a mixture of elements; (*d*) air is a mixture of compounds; (*e*) air is a mixture of elements and compounds?

9. Are the injurious effects resulting from poor ventilation due to (*a*) lack of oxygen? (*b*) excess of carbon dioxide? (*c*) high temperature? (*d*) too much moisture?

10. (*a*) Name a gas that is easily liquefied. (*b*) Name the one that is the most difficult of all to liquefy.

11. Of what is liquid air essentially composed?

12. (*a*) What is the name of the kind of vessels in which liquid air is kept? (*b*) Why are such vessels better than ordinary flasks?

THOUGHT QUESTIONS

1. Name (*a*) the discoverer and (*b*) the date of discovery of each of the elements present in the air.

2. Why is the atmosphere densest at the earth's surface?

3. Since oxygen, like water, can be obtained in the form of a gas, a liquid, or a solid, why do we say that water is a liquid and that oxygen is a gas?

4. What phenomenon would account for the presence of ozone in the atmosphere?

5. When an open vessel containing liquid air is placed on a cake of ice, the liquid air boils violently. Explain.

6. Carbon dioxide is much the heaviest of the gases present in the air. Why does it not settle to the ground?

7. Show how it is possible for the carbon in the coal which we burn to return to us as a constituent of bread or of meat.

8. A tube containing calcium chloride weighed 30.1293 g. A volume of air which weighed 15.2134 g. was passed through the tube, after which the tube and contents weighed 30.3405 g. Find the percentage of moisture in the sample of air.

FOR HONOR STUDENTS

1. Compare the boiling points of oxygen, nitrogen, and hydrogen (see Appendix F). When water boils, the hydrogen and oxygen pass off together, but when liquid air boils, the nitrogen passes off first. Account for this difference between liquid air and water.

2. Measure approximately in cubic meters the size of your classroom. Suppose that the air in the room is saturated with moisture and that the temperature is 20°. If now the temperature should fall to 10°, what weight of water would separate? (See § 272 for data.)

3. An average home using coal as a fuel burns about 12 tons of coal annually. Supposing that 80 per cent of the coal is carbon and that the combustion is perfect, what weight of carbon dioxide would be formed in the combustion of the 12 tons of coal? How many liters of carbon dioxide would be added to the atmosphere?

CHAPTER XXI

SOME OF THE SIMPLER COMPOUNDS OF NITROGEN

281. ***Introduction.*** Undoubtedly many of the elements are essential to life (§ 25). Among all of these nitrogen is regarded as one of the most important, since it is a necessary constituent of a group of compounds known as the *proteins,* which make up a large part of the living cells of all organisms. Our own bodies contain about 3 per cent of nitrogen, present chiefly in the form of proteins. Other nitrogen compounds are used as fertilizers, explosives, medicines, and dyes of various kinds, so that they are varied in character and important for our uses. At present we shall study only a few of the simpler ones.

Ammonia

282. General. Several compounds contain nothing but nitrogen and hydrogen; only one of these, ammonia (NH_3), need be considered. This is a colorless gas, and is formed when organic matter containing nitrogen decays, being especially noticeable about stables. It is well known to us, since its solution in water, technically called *aqua ammonia* or *ammonia water,* is sold by all grocers and druggists under the name of "ammonia." It is used in our homes as a cleansing agent and as a medicine.

283. Preparation of ammonia. Ammonia can be prepared in the laboratory by a simple method, but the industrial methods require elaborate apparatus.

1. ***Laboratory method.*** In the laboratory ammonia is prepared from ammonium chloride (NH_4Cl), a white solid obtained in the manufacture of coal gas. In this compound the group NH_4 acts as a univalent radical and is known as *ammonium.* When ammonium chloride is warmed with sodium hydroxide, *the ammonium radical and sodium change places,* the reaction being expressed in the following equation:

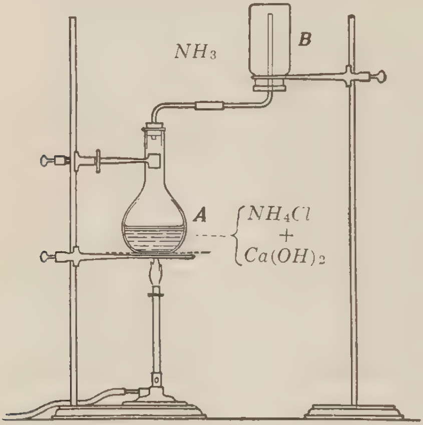


FIG. 134. Ammonium chloride and calcium hydroxide react when heated together and evolve ammonia, which is collected by displacing the air in the bottle *B*

$$NH_4Cl + NaOH \longrightarrow NaCl + NH_4OH$$

The ammonium hydroxide (NH_4OH) so formed is unstable and breaks down into water and ammonia:

$$NH_4OH \longrightarrow NH_3 + H_2O$$

Calcium hydroxide ($Ca(OH)_2$) is frequently used in place of the more expensive sodium hydroxide (Fig. 134), the equations being

$$2\ NH_4Cl + Ca(OH)_2 \longrightarrow CaCl_2 + 2\ NH_4OH$$
$$2\ NH_4OH \longrightarrow 2\ H_2O + 2\ NH_3$$

2. ***Commercial method.*** On a large scale ammonia is prepared by one of the two following methods:

(a) *By the direct combination of nitrogen and hydrogen — the Haber process.* When a mixture of nitrogen and hydrogen is heated or subjected to an electrical discharge, a small percentage of ammonia is formed. The small yield is due to the fact that some of the ammonia formed is decomposed again, and a balance or equilibrium between the formation of ammonia and its decomposition results, which may be expressed as follows:

$$N_2 + 3\,H_2 \rightleftarrows 2\,NH_3$$

The German chemist Haber found that the yield of ammonia could be greatly increased by applying a higher pressure to the mixture of gases and then heating this greatly compressed mixture in contact with a suitable catalyst. The method has been improved by others until now it furnishes nearly all the ammonia used in European countries and more than half of that used in the United States (Fig. 135).

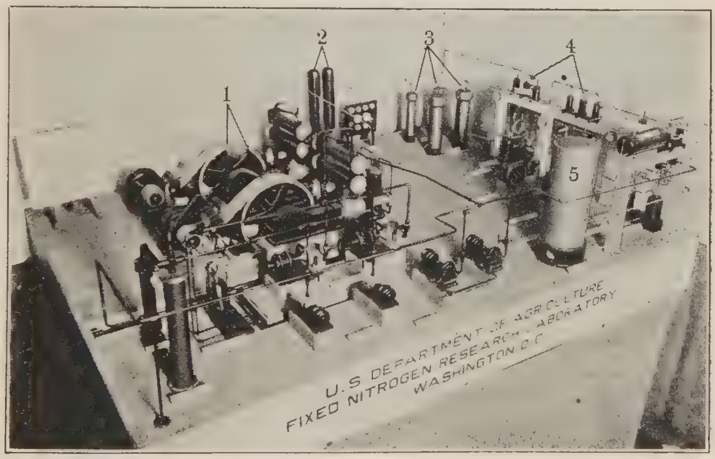

2
3
4
1
5
U.S. DEPARTMENT OF AGRICULTURE
FIXED NITROGEN RESEARCH LABORATORY
WASHINGTON D.C.

FIG. 135. A small model of a plant designed for the preparation of ammonia by the direct union of nitrogen and hydrogen

The nitrogen and hydrogen, mixed in the proportion of 1 volume of nitrogen to 3 of hydrogen, are compressed by engines marked 1. The compressed gases are then forced through the different tubes and cylinders marked 2, 3, and 4, which contain materials for purifiying the gases and a suitable catalyst for causing the gases to combine. The resulting ammonia is stored in the container marked 5

(b) *From coal.* Ordinary soft coal contains small percentages of nitrogen and hydrogen along with the carbon. When such coal is heated in the absence of air, as is done in the

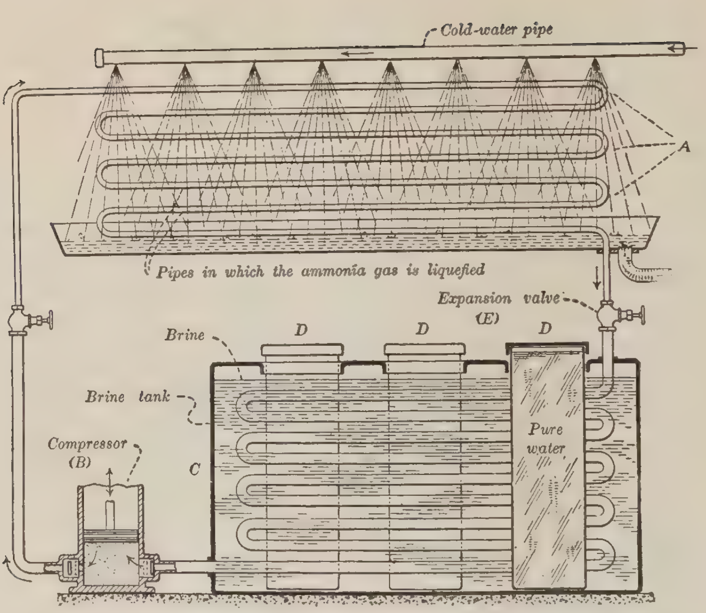


FIG. 136. Drawing illustrating the principle of the ammonia ice machine

Ammonia is compressed by means of a compressor pump *B* and led into the pipes *A*. A great deal of heat is liberated in this process, just as heat is liberated when air is pumped into a tire. This heat is absorbed by sprays of cold water flowing over the pipes as shown in the drawing. Through the combined effect of the pressure and cold, the ammonia is liquefied. The pipes in which the ammonia is liquefied lead into coils in a large tank *C*, nearly filled with brine, which is prepared by dissolving calcium chloride in water. Such a brine may be cooled quite a little below zero without freezing. By means of an expansion valve *E* the pressure upon the liquid ammonia is diminished as it enters the coils. As a result of this decrease in pressure, the liquid ammonia rapidly passes again into the gaseous state, a large amount of heat being absorbed in the process (§ 71). The heat so absorbed is taken from the brine in *C*, with the result that the temperature of the brine is lowered below 0°. Metal vessels *D*, *D*, *D*, filled with pure water, are lowered into the cold brine and left until the water in them is frozen into cakes of ice. The gaseous ammonia is led back to the compressor pump and again liquefied

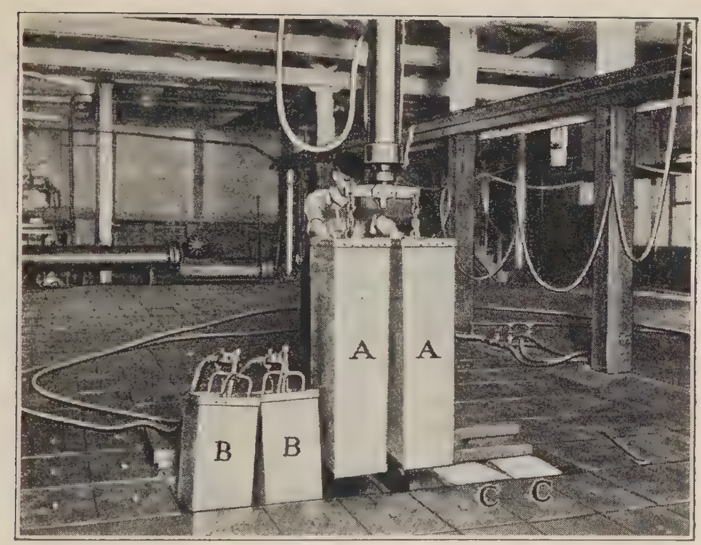


FIG. 137. View of the interior of an ice plant

Fig. 136 illustrates the principle of the ammonia ice machine, while Fig. 137 gives a view of the ice plant in actual operation. The floor is made up of small wooden plates, each one forming the cover of one of the metal vessels in which the water is frozen. These vessels are immersed to their rim in the brine tank under the floor. The picture shows two of these vessels, *A*, *A*, being withdrawn from the brine. The water in these is frozen and the cakes of ice in them are removed by immersing them for a short time in warm water and then inverting them. The vessels are then filled with distilled water, again immersed in the brine, and left until the water is frozen. The picture also shows two vessels *B*, *B*, from which the ice has just been removed, being filled with water. As the water flows in through the hose at the top, the vessels gradually sink into the brine. The tops of two other vessels, *C*, *C*, are also shown. The water in these is frozen and the ice is ready to be withdrawn. Refrigerating and cold-storage plants are operated on the same principle as the ice plants, except that the pipes containing the cold compressed ammonia are located in coils about the walls of the rooms. As the pressure is relieved, the heat absorbed reduces the temperature of the room to the desired point manufacture of coke and coal gas, a part of the nitrogen and hydrogen present combine to form ammonia. This is separated from the other compounds formed and is either dissolved in water, forming the *aqua ammonia* of commerce, or absorbed in acids, with which it forms solid compounds of great value, especially as fertilizers. Much of the ammonia used in the United States comes from this source.

284. Physical properties. Ammonia is a colorless gas and has a strong, suffocating odor. It is just about half as heavy as air. It is easily condensed to a colorless liquid, boiling at – 33.3°. This liquid, contained in strong steel cylinders, is a common article of commerce, and is used in large quantities for the manufacture of artificial ice (§ 286).

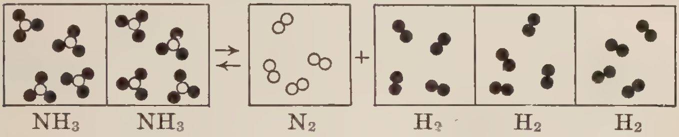
Ammonia is very soluble in water. At the normal pressure of the atmosphere (barometer at 760 mm.), 1 liter of water dissolves 1298 liters of the gas at 0°, and 710 liters at 20°. In dissolving such large volumes of the gas the water expands, so that the density of the solution is less than that of the water. The most concentrated commercial solutions have a density of about 0.88 and contain approximately 35 per cent by weight of the gas.

285. Chemical conduct. Ammonia will not support combustion nor will it burn under ordinary conditions. In an atmosphere of oxygen it burns with a feeble yellowish flame. When quite dry it is not a very active substance, but when moist it combines with a great many substances, particularly with acids.

286. Uses. As we have seen, ammonia can be condensed to a liquid by the application of a moderate pressure. If the pressure is removed, this liquid rapidly passes again into the gaseous state, and in so doing absorbs a great deal of heat. Advantage is taken of this fact in the manufacture of ice (Figs. 136, 137) and in keeping the temperature low in cold-storage plants. These are the chief uses of ammonia.

Large quantities of ammonia are also used in the manufacture of a variety of important compounds.

287. Composition of ammonia. It is possible to decompose a given volume of ammonia, and to measure the volumes of nitrogen and hydrogen obtained. In this way we find that 2 volumes of ammonia yield 1 volume of nitrogen and 3 volumes of hydrogen. These facts are illustrated in Fig. 138, in which the atoms of hydrogen are represented by black circles, and those of nitrogen by white ones:



2 vols. of $NH_3 \rightleftarrows$ 1 vol. of N_2 + 3 vols. of H_2

FIG. 138

288. Ammonium hydroxide (NH_4OH). Neither perfectly pure ammonia nor water has basic properties; yet when ammonia is dissolved in water the resulting solution has strong basic properties, turning red litmus blue and neutralizing acids to form salts. It is certain, therefore, that the ammonia and water when brought together react to form a base. Experiments have shown that this base has the composition NH_4OH, and that it is formed in accordance with the following equation:

$$NH_3 + H_2O \longrightarrow NH_4OH$$

This compound contains the ammonium radical, NH_4, and is called *ammonium hydroxide,* just as NaOH is called *sodium hydroxide.* It will be noticed that the ammonium radical *plays the part of a metal,* since its hydroxide is a *base.*

Ammonium hydroxide cannot be obtained in a pure state, because it is unstable when concentrated, decomposing into the compounds from which it is formed, namely, water and ammonia. *The solution of ammonia in water,* *therefore, constitutes a state of equilibrium between ammonia and water on the one hand and ammonium hydroxide on the other, as expressed in the following equation:*

$$NH_3 + H_2O \rightleftharpoons NH_4OH$$

289. Ammonium salts. Ammonium hydroxide as a base neutralizes acids, forming salts, which are called *ammonium* salts. Thus, hydrochloric acid with ammonium hydroxide reacts in the same way as does sodium hydroxide, as shown in the two equations

$$NH_4OH + HCl \longrightarrow NH_4Cl + H_2O$$
$$NaOH + HCl \longrightarrow NaCl + H_2O$$

The resulting salt, NH_4Cl, is called *ammonium chloride* just as NaCl is called sodium chloride.

290. Test for ammonium salts. When any ammonium salt is warmed with sodium hydroxide, ammonia gas is given off:

$$(NH_4)_2SO_4 + 2\ NaOH \longrightarrow Na_2SO_4 + 2\ H_2O + 2\ NH_3$$

The gas is easily recognized by its odor and by the fact that it will turn moistened red litmus paper blue. This makes a good test for ammonium salts.

Acids of Nitrogen

291. General. Nitrogen combines with hydrogen and oxygen to form a number of acids. Of these, nitric acid (HNO_3) is by far the most important. It is a liquid, very active as an acid, and hence never found free in nature. Some of its salts occur in nature, especially sodium nitrate ($NaNO_3$), or Chile saltpeter (§ 260).

292. Hydrogen nitrate and nitric acid (HNO_3). If we wish to be very exact, we must distinguish between hydrogen nitrate and nitric acid. The former is pure HNO_3; the latter is a *solution* of hydrogen nitrate in water. Hydrogen nitrate itself is very difficult to prepare because it is unstable; its solution in water, however, is easily obtained and constitutes one of our most important acids. The concentrated nitric acid of commerce contains about 68 per cent of hydrogen nitrate, 32 per cent of water, and in density is 1.4. When pure it is a colorless liquid, but it is often colored slightly brown by products of decomposition.

293. Preparation. Nitric acid is ordinarily prepared in the laboratory by the action of sulfuric acid on sodium nitrate ($NaNO_3$). When cold concentrated sulfuric acid is poured upon sodium nitrate no chemical action seems to take place. If, however, the mixture is heated in a retort *A* (Fig. 139), nitric acid is given off as a vapor and may easily be condensed to a liquid by passing the vapor into a tube *B* surrounded by cold water. An examination of the liquid left in the retort shows that it contains sodium hydrogen sulfate ($NaHSO_4$), only one of the two atoms of hydrogen in sulfuric acid having been replaced by sodium. The reaction may be represented by the equation

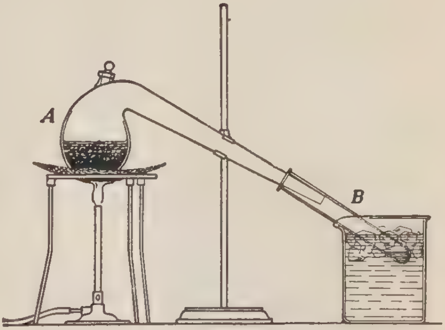


FIG. 139. Preparing nitric acid in the laboratory by the action of sulfuric acid on sodium nitrate

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$$

This reaction is also used for preparing nitric acid on a large scale, and much of the acid used in the United States is prepared in this way. Various types of apparatus are used, one of the most common being shown in Fig. 140.

294. Preparation of nitric acid from the nitrogen of the air. Since the supply of sodium nitrate is gradually diminishing and is so largely limited to one country, many efforts have been made to find a way of making nitric acid from the nitrogen of the air. There are two general ways of doing this: (1) The first consists in passing an electrical discharge through a mixture of nitrogen and oxygen. As a result oxides of nitrogen are produced which unite with

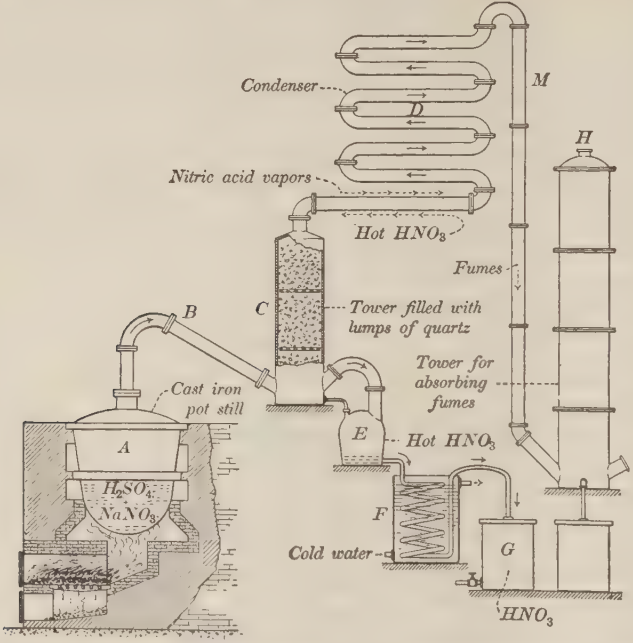

Condenser
D
M
H
Nitric acid vapors
Hot HNO_3
Fumes
B
C
Tower filled with lumps of quartz
Tower for absorbing fumes
Cast iron pot still
A
H_2SO_4
$NaNO_3$
E
Hot HNO_3
F
Cold water
G
HNO_3

FIG. 140. Diagram of apparatus used for preparing nitric acid on a large scale from sulfuric acid and sodium nitrate

The sulfuric acid and sodium nitrate are heated in the iron pot *A*. The resulting acid vapors pass, in the direction indicated by the arrows, upward through the tower *C* into the condenser tubes *D*, where they are condensed. These tubes are inclined so that the nitric acid resulting from the condensation of the vapors runs back through the tower *C* into the vessel *E*. The acid is cooled by cold water in *F* and finally collects in the vessel *G*, from which it is drawn off. Any vapors not condensed in *D* pass down through the pipe *M* and are absorbed in the tower *H* water to form nitric acid. This method is used in Norway, where the waterfalls make cheap electrical energy possible. (2) The better method consists in first converting the nitrogen of the air into ammonia. This can be done either by the Haber process (§ 283, 2 (a)) or by a process which will be described later under the heading "Cyanamide." If the ammonia mixed with air is then passed over a catalytic agent (platinum is used) in a heated tube, nitric acid is formed through the oxidizing action of the air. The reaction is very complex, but it may be represented as follows:

$$NH_3 + 2\,O_2 \longrightarrow HNO_3 + H_2O$$

This is the chief method used both in European countries and in the United States for the manufacture of nitric acid on a large scale.

295. Chemical conduct. The important reactions of nitric acid are as follows:

1. ***Acid properties.*** Nitric acid has all the characteristics of a strong acid, changing the color of indicators and forming salts with bases.

2. ***Oxidizing action.*** Nitric acid is not so stable as hydrochloric acid. When heated or when exposed for some time to the sunlight it undergoes partial decomposition, forming water and the two gases nitrogen dioxide and oxygen. Because of these facts nitric acid is a good oxidizing agent. It has a peculiar action upon the skin, turning it yellow.

3. ***Action on metals.*** We have learned that when a metal which is above hydrogen in the electrochemical series (§ 256), such as zinc, is brought into contact with either sulfuric acid or hydrochloric acid, the metal takes the place of the hydrogen of the acid, forming a salt of the acid, while free hydrogen is evolved; this is the way we prepare hydrogen in the laboratory. We might expect that nitric acid would act in the same way, forming zinc nitrate ($Zn(NO_3)_2$) and hydrogen, thus:

$$Zn + 2\,HNO_3 \longrightarrow Zn(NO_3)_2 + H_2 \qquad (1)$$

When we try the experiment, however, we find no hydrogen evolved, but instead another gas named nitric oxide (NO). The reason is very clear, for nitric acid is a strong oxidizing agent, while hydrogen, especially in the nascent state (§ 217), is an equally strong reducing agent; so that any hydrogen set free according to equation (1) will not be evolved but will be oxidized to water by the nitric acid, thus:

$$3\ H + HNO_3 \longrightarrow 2\ H_2O + NO \qquad (2)$$

If we study equations (1) and (2), we find that the products of the reaction between zinc and nitric acid are, then, zinc nitrate, water, and nitric oxide, and we may express this reaction in a single equation as follows:

$$3\ Zn + 8\ HNO_3 \longrightarrow 3\ Zn(NO_3)_2 + 4\ H_2O + 2\ NO$$

Metals *below hydrogen* in the electrochemical series ordinarily do not react with acids. Nitric acid, however, being a strong oxidizing agent, oxidizes the metals, converting them into oxides, which then dissolve in the acid to form nitrates. With copper, for instance, the general reaction is expressed in the equation

$$3\ Cu + 8\ HNO_3 \longrightarrow 3\ Cu(NO_3)_2 + 4\ H_2O + 2\ NO$$

296. Aqua regia. What reaction, if any, should we expect to take place when nitric acid and hydrochloric acid are mixed? Since nitric acid readily gives up oxygen, we should expect this oxygen to combine with the hydrogen of the hydrochloric acid, liberating chlorine — and this is what actually takes place. This mixture of nitric and hydrochloric acids was well known to the alchemists, who called it *aqua regia* ("royal water") because it dissolved gold, the king of metals. We still use this name.

Aqua regia is a very powerful solvent, not because it is an acid but *because it sets free nascent chlorine.* Metals such as gold and platinum, which are not soluble in any common acid, readily dissolve in aqua regia, being converted into chlorides by its action.

297. Uses. Nitric acid has countless uses in the industries and in chemical laboratories. It is most extensively used in the manufacture of explosives of various kinds and of celluloid, photographic films, and dyes.

298. Salts of nitric acid: nitrates. The salts of nitric acid are called *nitrates*. Many of these salts will be described in the study of the metals. They are all solids soluble in water, and, when heated to a high temperature, undergo decomposition. The nitrates are most largely used in the manufacture of gunpowder, sulfuric acid, and nitric acid, and as a fertilizer.

299. Test for nitrates. Through a complicated reaction nitric acid produces a nearly black color when added to a solution of ferrous sulfate ($FeSO_4$). A delicate test for the presence of a nitrate in a solution is based on this fact as follows:

To a solution in a test tube, suspected of containing a nitrate, is added a solution of ferrous sulfate. Concentrated sulfuric acid is then carefully poured into the test tube (held in a slanting position) in such a way as to run down the inside of the tube and collect on the bottom without mixing with the solution. A brown ring forms between the heavy sulfuric acid and the lighter solution (containing the nitrate) floating on top.

300. Nitrous acid (HNO_2). It is an easy matter to obtain sodium nitrite ($NaNO_2$) by heating sodium nitrate with lead:

$$NaNO_3 + Pb \longrightarrow NaNO_2 + PbO$$

Now when sodium nitrite is treated with an acid, such as sulfuric acid, it is decomposed, and nitrous acid is set free:

$$NaNO_2 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_2$$

The acid is very unstable, however, and decomposes into water and oxides of nitrogen. Sodium nitrite is used in the manufacture of dyes.

Oxides of Nitrogen

301. OXIDES OF NITROGEN

Name	Formula	Description
Nitrous oxide	N_2O	A colorless gas
Nitric oxide	NO	A colorless gas
Nitrogen dioxide	NO_2	A reddish-brown gas
Nitrogen trioxide	N_2O_3	Known only at low temperatures
Nitrogen pentoxide	N_2O_5	A white solid

302. Nitrous oxide (laughing gas) (N_2O). This gas is most readily prepared by heating ammonium nitrate:

$$NH_4NO_3 \longrightarrow 2\,H_2O + N_2O$$

It is colorless, is somewhat soluble in water, and in solution has a slightly sweetish taste. When inhaled it produces a kind of hysteria (hence the name *laughing gas*) and, if taken in large amounts, insensibility to pain and unconsciousness. It was the first substance to be used as an anæsthetic in surgery, and it is still used in minor operations, such as those of dentistry (Fig. 141).

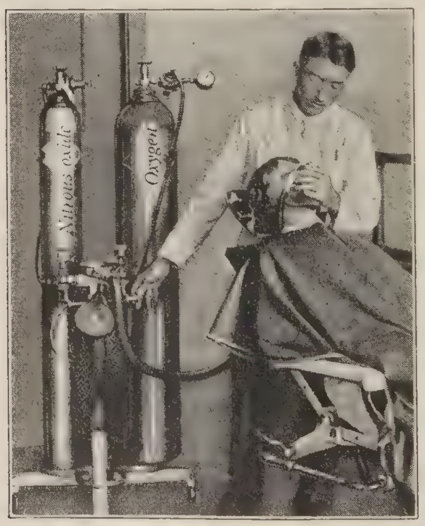


FIG. 141. Administering laughing gas mixed with oxygen in a dental operation

Nitrous oxide is a very energetic oxidizing agent. Substances such as carbon, sulfur, iron, and phosphorus burn in it almost as brilliantly as in oxygen, forming oxides and setting free nitrogen. Evidently the oxygen in nitrous oxide is not held in very firm combination by the nitrogen.

303. Nitric oxide (NO). Nitric oxide is most conveniently prepared by the action of nitric acid upon copper (Fig. 142):

$$3\ Cu + 8\ HNO_3 \longrightarrow 3\ Cu(NO_3)_2 + 4\ H_2O + 2\ NO$$

It is a colorless, poisonous gas, and, unlike nitrous oxide, does not give up its oxygen readily, so that the flames of burning substances introduced into the gas are usually extinguished.

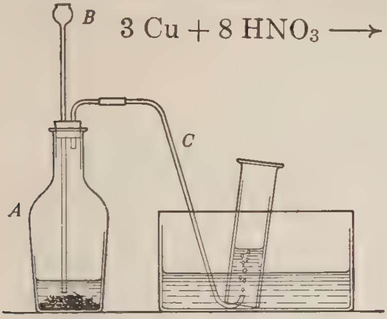


FIG. 142. Preparation of nitric oxide

Copper turnings are placed in the bottle *A* and nitric acid is added through the funnel tube *B*. Nitric oxide escapes through *C* and is collected over water

304. Nitrogen dioxide (NO_2). When nitric oxide comes into contact with oxygen or air, it at once combines with the oxygen (Fig. 143), even at ordinary temperatures, forming *nitrogen dioxide* (NO_2):

$$2\ NO + O_2 \longrightarrow 2\ NO_2$$

It is a reddish-brown gas of unpleasant odor and is very poisonous when inhaled.

305. Acid anhydrides. The oxides N_2O_3 (nitrogen trioxide) and N_2O_5 (nitrogen pentoxide) are rarely prepared and so they will not be separately described. They bear a very interesting relation to the acids of nitrogen. When dissolved in water they combine with the water, forming acids:

$$N_2O_3 + H_2O \longrightarrow 2\ HNO_2$$
$$N_2O_5 + H_2O \longrightarrow 2\ HNO_3$$

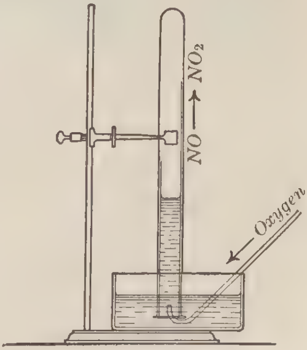


FIG. 143. The formation of nitrogen dioxide from nitric oxide and oxygen

These oxides belong to a very important group of compounds known as *acid anhydrides.* This group may be defined as follows: *An acid anhydride is an oxide which combines with water to form an acid.*

Compounds of Nitrogen with Carbon

306. Cyanogen (C_2N_2); hydrogen cyanide (HCN); hydrocyanic acid. At high temperatures carbon unites with nitrogen to form the colorless, very poisonous gas known as cyanogen (C_2N_2). With hydrogen and nitrogen it forms hydrogen cyanide (HCN), a colorless liquid boiling at 26°. Hydrogen cyanide vapor has the odor of peach kernels. *It is one of the most poisonous compounds known,* and is used to destroy insects, especially those on citrus fruit trees, such as lemon and orange trees (Fig. 144). When dissolved in water hydrogen cyanide forms a *very weak acid* known as *hydrocyanic acid* or *prussic acid.* Its salts are called *cyanides.*

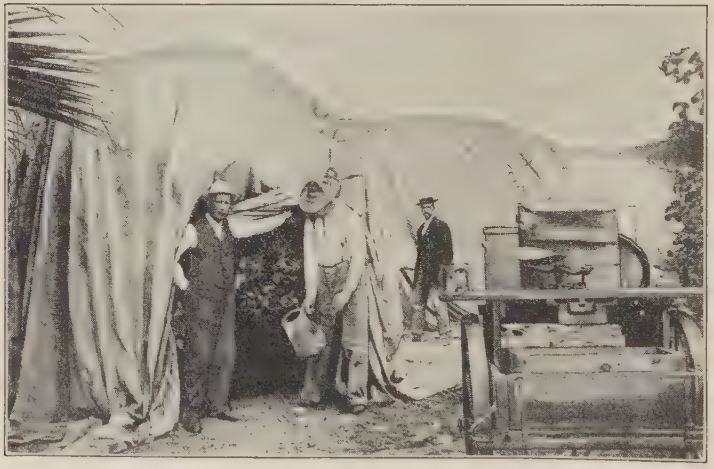


FIG. 144. Fruit trees covered with cloths under which hydrogen cyanide is being liberated to kill insect pests

Sodium cyanide (NaCN) is a white solid; its solution dissolves gold, hence it is used in extracting gold from its ores. It is also used to kill butterflies and beetles for museum collections. The acid and all its salts are very poisonous.

CHAPTER SUMMARY IN QUESTION FORM

1. (*a*) What is aqua ammonia? (*b*) For what is it used?

2. (*a*) Name the two compounds that are used in preparing ammonia in the laboratory. (*b*) Write the equation for the reaction that takes place when these compounds are heated together. (*c*) How is the gas collected?

3. What is the principal source of the ammonia used commercially (*a*) in the United States? (*b*) in European countries?

4. Fill in the missing words: Ammonia is a ------ gas, and has a ------ odor. It is very soluble in ------, forming ------ ------.

5. Write the equation for the reaction that takes place when ammonia is brought into contact with water.

6. Show how ammonia makes possible the manufacture of artificial ice.

7. State what each of the following words represents: (*a*) ammonia; (*b*) ammonium.

8. Write the formulas for each of the following salts: (*a*) ammonium chloride; (*b*) ammonium sulfate; (*c*) ammonium nitrate.

9. Suppose you had a white solid and wished to know if it was an ammonium salt. How would you proceed to test it?

10. Give the name and formula of the compound whose solution in water is called nitric acid.

11. (*a*) What two compounds react to form nitric acid? (*b*) Write the equation.

12. What is the chief method used for preparing nitric acid (*a*) in the United States? (*b*) in European countries?

13. Aside from its acid properties, what is the chief chemical characteristic of nitric acid?

14. (*a*) What name is applied to a mixture of hydrochloric acid and nitric acid? (*b*) Account for the fact that neither hydrochloric acid nor nitric acid will dissolve gold, yet a mixture of the two will dissolve it.

15. (*a*) What name is given to the salts of nitric acid? (*b*) Mention three properties common to such salts.

16. How could you test for the presence of such salts?

17. (*a*) Give two names for the compound represented by the formula N_2O. (*b*) How is it prepared? (*c*) For what is it used?

18. Copper is dissolved in nitric acid. (*a*) What becomes of the copper? (*b*) What gas is evolved? (*c*) What compound forms when this gas comes into contact with air?

19. What name is applied to oxides that combine with water to form acids?

20. (*a*) Give the name and formula for one of the most poisonous compounds known. (*b*) For what is it used?

THOUGHT QUESTIONS

1. Give the method used in collecting each of the following gases when prepared in the laboratory: (*a*) hydrogen; (*b*) oxygen; (*c*) nitrogen; (*d*) chlorine; (*e*) hydrogen chloride; (*f*) carbon dioxide; (*g*) ammonia.

2. Why is ammonia used in making artificial ice, rather than some other gas such as air?

3. What compounds are present in aqua ammonia?

4. From the standpoint of the theory of ionization, what ions must be present in aqua ammonia?

5. Write three different equations, each representing the formation of an ammonium salt.

6. What compounds are formed when an electric discharge is passed through a mixture of (*a*) nitrogen and hydrogen? (*b*) nitrogen and oxygen in the presence of water?

7. All nitrates are soluble. Are all chlorides soluble?

8. What substances have we studied that might be formed during a thunderstorm?

9. Hydrogen is evolved when zinc is dissolved in either hydrochloric acid or sulfuric acid, but not when zinc is dissolved in nitric acid. Explain.

10. Calculate the number of liters of (*a*) hydrogen and of (*b*) nitrogen required to prepare 1000 liters of ammonia by the Haber process.

11. The temperature of your laboratory is about 20°. If the barometer reading is 760 mm. (thus indicating a standard pressure), (*a*) calculate the number of liters of ammonia required to saturate 1 liter of water in the laboratory (see § 284 for data). (*b*) What is the approximate weight of this volume of ammonia? (*c*) What weight of ammonium chloride will be required for its preparation?

12. Suppose you were a manufacturing chemist and received an order for 100 liters of nitrous oxide. (*a*) What compound would you use in making it? (*b*) What weight of this would be required?

FOR HONOR STUDENTS

1. Read Chapter II of Slosson's "Creative Chemistry" (entitled "Nitrogen — Preserver and Destroyer of Life"), and write a brief review of it.

2. Show by diagrams how it happens that 3 volumes of hydrogen and 1 volume of nitrogen, on combining, form only 2 volumes of ammonia.

3. Suppose you had five bottles filled, respectively, with ammonia, nitric oxide, nitrous oxide, carbon dioxide, and hydrogen. How could you distinguish any one from the others?

4. Copper is below hydrogen in the electrochemical series, yet it readily reacts with nitric acid. Explain, illustrating by equations.

CHAPTER XXII

REVERSIBLE REACTIONS; EQUILIBRIUM

Reactions that go in Either Direction

307. ***Introduction.*** If we start the engine of an automobile and throw in one set of gears, the car moves forward; if we throw in another set of gears it reverses its direction and moves backward. The car can go forward or backward, but it cannot move in both directions at the same time, *because it is an individual.* To move in both directions the individual must change his direction.

If we watch the cars passing in the street we at once see that they *are* going in opposite directions at the same time, *because there are numbers of them.* Each individual car goes one way only, but taken collectively they are going in both directions.

If we should be interested in some specific detail of the cars passing in the street — their direction, their color, their make, their number of cylinders — we should soon stop recording the numbers in actual figures and express them in percentages. *On the average,* 40 per cent go in one direction and 60 per cent in the opposite direction; or 50 per cent are black, 50 per cent are colored, and of the latter we could further work out the percentage of each of the various colors. These results would be called *statistical.* They would be *average* figures for a very large number of individual cases.

Now the chemist is rarely concerned with the *individual* molecules in a reaction, but with *vast numbers* of them; so all his conclusions are of a statistical character.

308. Reversible reactions. In a number of cases we have studied reactions that were described as capable of going in either direction. Thus, in the Haber process (§ 283, 2, (a)) nitrogen and hydrogen combine to form ammonia, but at the same time ammonia decomposes more or less rapidly into nitrogen and hydrogen.

$$N_2 + 3\,H_2 \rightleftarrows 2\,NH_3$$

This does not mean that the reaction first goes one way for a time and then reverses, as a single automobile would do; but that in a mixture of nitrogen, hydrogen, and ammonia, molecules of nitrogen and hydrogen are here and there reacting to form ammonia, while at the same time molecules of ammonia are here and there decomposing. In automobile language, there is two-way traffic; this is what the double arrows ($\rightleftarrows$) indicate.

Similarly, when we dissolve ammonia in water, ammonium hydroxide is formed, which readily decomposes again into ammonia and water (§ 288):

$$NH_3 + H_2O \rightleftarrows NH_4OH$$

Reactions of this kind, which can go in either direction or in both directions at the same time, are called *reversible reactions.*

309. Objections. One might be inclined to argue that if, in a mixture of nitrogen and hydrogen, conditions are favorable for any molecules of the two gases to unite, they would be favorable for *all* molecules to unite; and if so, there would be no reason for ammonia molecules to decompose into nitrogen and hydrogen and at once unite again. This reasoning would be sound *if all the molecules in the gas mixture were under the same conditions.* But they are not. Some are moving with the speed of a rifle bullet, some very slowly; some are in violent collision, some in gentle collision, while some escape collision for a time. It is not then very surprising that in a gas mixture some molecules are being formed, while others are being knocked to pieces.

310. Equilibrium. If now we prepare a mixture of substances capable of taking part in a reversible reaction, and allow the reaction to go on for a time, it is evident that the two opposite reactions will presently become so adjusted to each other that *the changes in the one direction will just offset those in the other direction.* This balanced state of affairs is called *equilibrium.* The individual molecules will keep on reacting with each other, but in a statistical way the *average percentage* of each material present will remain unchanged. Thus, in the Haber process (§283, 2, (a)) a mixture of hydrogen and nitrogen, under a pressure of 200 atmospheres, at a temperature of 500°, and in contact with a suitable catalyst, comes to equilibrium when about 8 per cent of the nitrogen has been combined with hydrogen to form ammonia.

311. Mass action. Let us suppose an equilibrium has been reached between nitrogen, hydrogen, and ammonia as represented in the reversible equation

$$N_2 + 3\ H_2 \rightleftarrows 2\ NH_3$$

What will be the effect of suddenly adding more hydrogen to the mixture? This will not greatly affect the rate at which ammonia is decomposing, for that does not depend upon hydrogen. But it *will* affect the rate at which nitrogen is combining with hydrogen, because the nitrogen molecules will now meet with hydrogen molecules much oftener and this will favor their union. The net effect will therefore be to shift the point of equilibrium to a new one in which a greater proportion of ammonia to nitrogen is present. A similar change in equilibrium would result from increasing the nitrogen instead of the hydrogen. If nitrogen and hydrogen were both to be added *in the ratio in which they act together,* there would be no change in equilibrium. *The change in the point of equilibrium brought about by an excess of one of the reacting materials is called mass action.*

312. Bringing reversible reactions to completion. In the laboratory as well as in manufacturing operations we want to get as large a yield as possible from the materials we use, and a reaction that results in an equilibrium means a loss. Such reactions are avoided unless ways can be devised to break up the condition of equilibrium and bring the reaction to a definite completion.

If in a reversible reaction we can so arrange conditions that *one product of the reaction is removed as fast as it is formed,* then there can be no reverse reaction and therefore no equilibrium, and the reaction will go on to completion. Thus in the Haber process (§ 283, 2, (a)) we circulate the reaction mixture over water or sulfuric acid, *which removes the ammonia molecules,* and the reacting mixture can then produce more ammonia. *A reversible reaction may be changed into a completed reaction by removing one of the substances taking part in it as fast as it is formed.*

Let us take another example. Ordinary limestone is impure calcium carbonate ($CaCO_3$). When heated it decomposes into the solid known as lime (calcium oxide, CaO) and the gas carbon dioxide. If heated in a *closed* vessel equilibrium is soon reached:

$$CaCO_3 \rightleftarrows CaO + \overline{CO_2}$$

If heated in an *open* vessel, however, the carbon dioxide escapes as fast as formed, and the reaction goes to completion.

313. Equilibrium in solution. In aqueous solution the molecules of an electrolyte keep parting into ions, and the ions, on meeting, recombine to form molecules; the result is an equilibrium between the two conditions, thus:

$$HNO_3 \rightleftarrows H^+ + NO_3^-$$

If we mix *two* electrolytes the equilibrium reached becomes much more complicated, for *any positive ion* may unite with *any negative one.* Thus, when we mix sodium nitrate and sulfuric acid in the preparation of nitric acid, we have present the ions Na^+, NO_3^-, H^+, and SO_4^{--}, together with the molecules $NaNO_3$, Na_2SO_4, $NaHSO_4$, HNO_3, and H_2SO_4.

314. Completion of reactions in solutions. For the most part the chemist carries on his reactions in solutions (or in melted mixtures), and so he is especially interested in finding out the conditions that may be depended on to bring various reversible reactions in solutions to completion. *There are three general conditions which may be depended on to bring to completion a reversible reaction in solution.*

1. ***A volatile gas may be formed and escape.*** If the reaction is conducted under such conditions that one of the products is a gas *insoluble in the solvent*, the gas will make its escape as fast as it is formed, and this action will continue until one or the other of the ions taking part in its formation is used up.

Thus, when we mix sulfuric acid and sodium nitrate (§ 293) no visible reaction takes place at room temperature. But if we heat the mixture above the boiling point of nitric acid, then the nitric acid formed in the equilibrium between the H^+ and the NO_3^- ions is converted into a gas *insoluble in sulfuric acid* and distills away until the NO_3^- ions are used up. We then have a completed reaction expressed in the equation

$$Na^+, NO_3^- + H^+, HSO_4^- \longrightarrow Na^+, HSO_4^- + \overline{HNO_3} \text{ (gas)}$$

It is in this way that most acids are prepared. Most of them are rather low-boiling liquids. Their salts are heated *with some acid of high boiling point,* usually with sulfuric acid, which boils at 338°.

2. ***An insoluble solid may be formed and precipitated.*** When hydrochloric acid (HCl) and silver nitrate ($AgNO_3$) are brought together in solution we have in addition to these two compounds the ions H^+, Cl^-, Ag^+, NO_3^- and the new combinations HNO_3 and $AgCl$. *One of these,* namely, silver

chloride ($AgCl$), *is insoluble in water*; therefore as fast as it is formed, it separates from the solution as a curdy white *precipitate* (Fig. 145). The reaction therefore continues till either the Ag^+ or the Cl^- is used up, the completed equation being

$$H^+, Cl^- + Ag^+, NO_3^- \longrightarrow H^+, NO_3^- + \underline{AgCl} \text{ (solid)}$$

3. ***Two different ions may unite to form an un-ionized molecule.*** When we bring together sodium hydroxide and hydrochloric acid in solution, we have the ions H^+, Cl^-, Na^+, and OH^-. The H^+ ions and the OH^- ions unite to form molecules of water *which do not again part into ions* save to a very slight extent. This leaves only the ions of $NaCl$ in solution, the equation being

$$Na^+, OH^- + H^+, Cl^- \longrightarrow Na^+, Cl^- + H_2O$$

Neutralization is practically a completed reaction *because water is so little ionized* and when the ions OH^- and H^+ unite to form a water molecule they are *almost* completely removed from taking further part in a reaction.

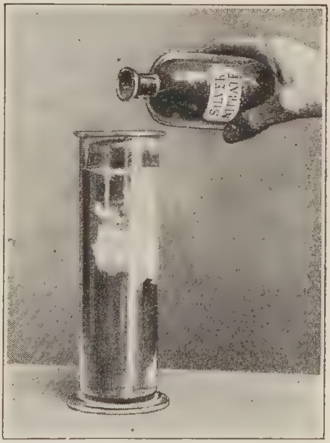


FIG. 145. Precipitating silver chloride by the action of silver nitrate on hydrochloric acid

315. The test for chloride ions. From what has been stated under condition 2 above, it is evident that the test which we used for the detection of hydrochloric acid and the chlorides (§ 221) is really a test for chloride ions. Both hydrochloric acid and the chlorides in solution respond to the test, for both give chloride ions when dissolved in water. To distinguish between hydrochloric acid and a chloride we must devise an additional test (§ 221).

CHAPTER SUMMARY IN QUESTION FORM

1. What name do we give to a reaction that goes in either direction?

2. What name do we apply to the condition that exists in a reaction when the change in the one direction just equals the change in the other?

3. To show how we represent a reversible reaction, write the equation (*a*) for the preparation of ammonia by the Haber process; (*b*) for the reaction between ammonia and water; (*c*) for the reaction between sodium chloride and the ions it forms when dissolved in water.

4. Suppose in the reaction represented by the equation

$$N_2 + 3\ H_2 \rightleftarrows 2\ NH_3$$

an equilibrium exists, what would be the effect of increasing (*a*) the amount of hydrogen present? (*b*) the amount of nitrogen present?

5. What term do chemists apply to the change in the point of equilibrium brought about by adding an excess of one of the reacting materials?

6. When heated in an open retort limestone is completely decomposed into calcium oxide and carbon dioxide, but it is not completely decomposed if the retort is closed. Explain.

7. (*a*) Is it possible in all reversible reactions taking place in solutions to bring the reaction to completion? (*b*) If not, name three conditions which, if they exist, will enable you to bring the reaction to completion.

8. When sodium nitrate is heated with sulfuric acid, the reaction goes to completion. Why?

9. When a solution of silver nitrate is added to hydrochloric acid, the reaction goes to completion. (*a*) Why? (*b*) Give the name and formula for each compound formed.

10. (*a*) Write the equation for the reaction between sodium hydroxide and hydrochloric acid, representing all the ions present. (*b*) Why does the reaction go to completion?

THOUGHT QUESTIONS

1. In preparing carbon dioxide by the action of hydrochloric acid on marble the reaction goes to completion without heating. In preparing nitric acid by the action of sulfuric acid on sodium nitrate (§ 293) it is necessary to heat the mixture. Why is heat necessary in the one case and not in the other?

2. If the substances represented below react, complete and balance the equation. If the reaction is reversible, indicate this fact in the usual way. Indicate in the usual way the gases and insoluble products formed. (See Table of Solubilities in Appendix D and Electrochemical Series in § 256 for certain data needed.)

(*a*) $Zn + H_2SO_4$
(*b*) $NaNO_3 + H_2SO_4$
(*c*) $AgNO_3 + KCl$
(*d*) $HCl + Ag$
(*e*) $NaOH + HNO_3$
(*f*) $BaCl_2 + H_2SO_4$
(*g*) $Ca(OH)_2 + CO_2$
(*h*) $Na_2CO_3 + HCl$
(*i*) $HCl + H_2O$
(*j*) $ZnCl_2 + Cu$
(*k*) $AgNO_3 + Cu$
(*l*) $Na_2SO_4 + Zn$
(*m*) $NaNO_3 + KCl$
(*n*) $H_2SO_4 + H_2O$
(*o*) $NaOH + NH_4Cl$
(*p*) $KNO_3 + Cu$

FOR HONOR STUDENTS

1. One of the preparations used for destroying germs of fungous diseases on trees is made by adding a solution of copper sulfate ($CuSO_4$) to calcium hydroxide ($Ca(OH)_2$) in a tank of water. (*a*) Is there any objection to dissolving the copper sulfate in an iron kettle? (*b*) Write an equation representing the equilibrium between the copper sulfate and its ions when dissolved in water. (*c*) Do you think any reaction will take place between the copper sulfate and calcium hydroxide? Give your reasons.

2. Suggest conditions for making the reaction represented below go in either direction:

$$NH_3 + H_2O \rightleftarrows NH_4OH$$

3. Barium sulfate ($BaSO_4$) is a white insoluble compound used in paints. Suppose you had a supply of barium chloride ($BaCl_2$) and wished to convert it into barium sulfate. Suggest one or more methods for doing this, and explain the reactions.

CHAPTER XXIII

SULFUR AND THE SULFIDES

A Familiar Element with Many Uses

316. ***Introduction.*** Most people are sufficiently familiar with sulfur to recognize the yellow solid when they see it, but few understand its extreme importance to civilization both in peace and in war. In peace we depend upon its compounds for important insecticides to protect fruit and vegetables from insect ravages, for the refining of petroleum, and for the manufacture of soap, paper, matches, explosives for mining coal, dynamite for blasting rocks and making roads, and rubber for automobile tires and a host of other articles. In war we must add to this list the manufacture of nearly all explosives and of mustard gas. It is clear that it is a most important element.

Sulfur

317. General. Sulfur is one of the elements known from very early times. It is the brimstone of the Bible; it played a notable part in the speculations of the alchemists as to the nature of matter and its compounds.

318. Occurrence. Sulfur is widely distributed in nature and occurs in large quantities in the uncombined form, especially in the neighborhood of volcanoes. It is occasionally found in well-formed crystals (Fig. 146). The United States is by far the greatest sulfur-producing country, and Texas produces approximately 99 per cent of its output — about 1,500,000 tons annually. Sicily has long been

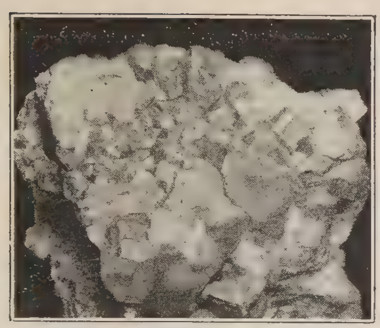


FIG. 146. Crystals of rhombic sulfur as they are found in nature

famous for its sulfur mines, and Japan, Mexico, and Greece have rich deposits.

In combination, sulfur occurs abundantly, combined with metals as sulfides and sulfates; in smaller amounts it is found in a great variety of minerals and is a constituent of many vegetable and animal substances, especially of eggs.

319. Extraction of sulfur. In Texas (and in Louisiana) the sulfur occurs in deposits far underground and is covered with quicksand so that it cannot be mined. A typical deposit lies at a depth of 700 ft.; it is circular in shape, and is about half a mile in diameter and 500 ft. in thickness. For years there seemed to be no way to get at these vast stores of sulfur, but about 1900 the American engineer Frasch solved the problem in a very ingenious way.

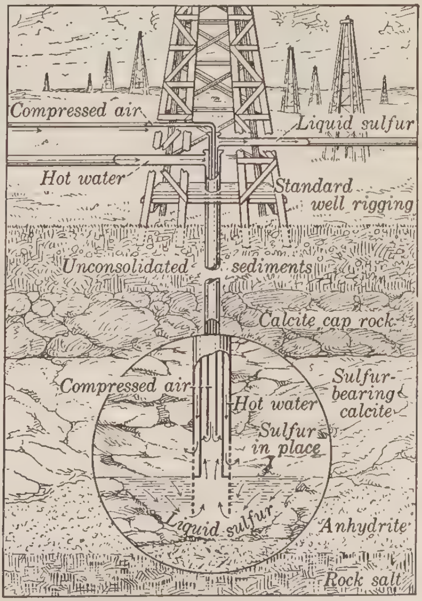

Compressed air
Liquid sulfur
Hot water
Standard well rigging
Unconsolidated sediments
Calcite cap rock
Compressed air
Hot water
Sulfur-bearing calcite
Sulfur in place
Liquid sulfur
Anhydrite
Rock salt

FIG. 147. Diagram of the Frasch process

Wells are drilled into the deposit, and superheated water (approximately 180°) is forced down through suitable pipes (Fig. 147). The hot water not only melts the sulfur but, being under pressure, forces the molten sulfur to the earth's surface through pipes suitably arranged. Hot air is also forced into the well to work the sulfur into a light foam and assist in lifting it. The liquid sulfur then solidifies in very large blocks (Fig. 148). A single well has produced 500 tons daily, and the product is 99.5 per cent pure. The production is limited only by the market demand.

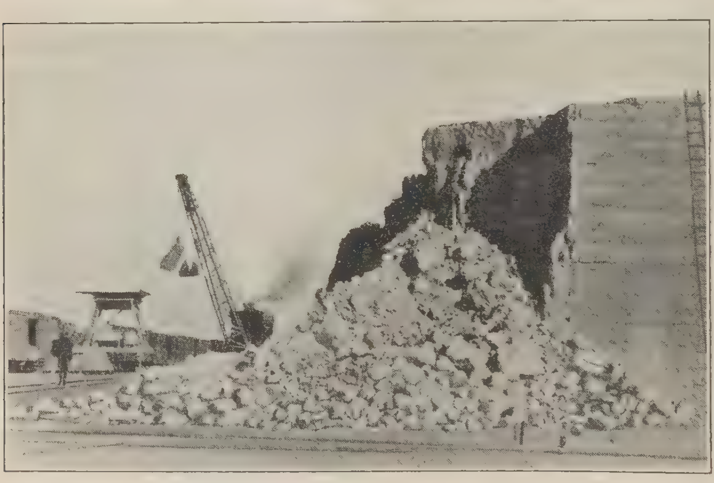


FIG. 148. A block of sulfur at the mine

320. Distillation of sulfur. Prior to the development of the Frasch process, crude sulfur was imported from Sicily and purified by distillation. When the sulfur vapor first enters the cold condensing chamber, it condenses as a fine crystalline powder called *flowers of sulfur*. As the condensing chamber becomes warm the sulfur condenses as a liquid and is drawn off into cylindrical molds, the product being called *roll sulfur* or *brimstone*.

321. Physical properties. Ordinary sulfur is a pale-yellow solid without marked taste, and with but a faint odor. It is a nonconductor of electricity, is insoluble in water, but is freely soluble in a few liquids, notably carbon disulfide. It melts when heated and forms a rather thin, straw-colored liquid. If this liquid is heated carefully, it turns darker in color as the temperature rises, and becomes thicker until at about 235° it is almost black and is so thick that the vessel containing it can be turned upside down without danger of having the liquid run out. At higher temperatures it becomes thin once more and boils at 444.6°, forming a yellowish vapor. When the vapor cools the same changes take place in the reverse order.

322. Varieties of sulfur. Sulfur exists in a number of quite different (allotropic) forms. Many other elements occur in a number of different forms (§ 56), but those of sulfur are unusually numerous and are easy to obtain. The best-known are the following:

1. ***Ordinary, or rhombic, sulfur.*** When sulfur crystallizes from solution in liquids (notably from carbon disulfide) it is obtained in compact yellow crystals which melt at 112.8°. This is called *rhombic sulfur.* Brimstone and the crystals found in nature are composed largely of this variety (Fig. 146).

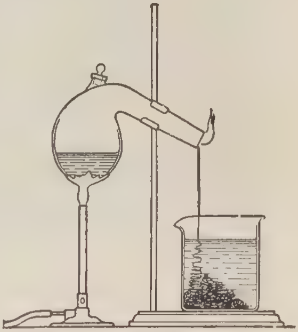


FIG. 149. Plastic sulfur is prepared by distilling sulfur and chilling the condensed liquid in water

2. ***Prismatic, or monoclinic, sulfur.*** When melted sulfur is allowed to cool until a part of the liquid has solidified, and the remaining liquid is then poured off, it is found that the solid sulfur remaining in the vessel is in the form of fine needle-shaped crystals which melt at 119.2°. The needle-shaped form is called *monoclinic sulfur.* At all temperatures below 96° the needle-shaped crystals break up more or less rapidly into little crystals of the rhombic variety.

3. ***Plastic sulfur.*** When boiling sulfur is poured into cold water it assumes a gummy, doughlike form which is quite elastic (Fig. 149). It is simply undercooled (§ 76) liquid sulfur. In a few days it passes over into ordinary rhombic sulfur.

323. Chemical conduct of sulfur. Sulfur burns in oxygen or in the air with a pale-blue flame, forming sulfur dioxide (SO_2). When heated with metals, sulfur combines directly with them, forming metallic sulfides. In some cases the action is so energetic that the mass becomes incandescent, as is the case with iron. This conduct recalls the action of oxygen upon metals, and in general the metals which combine readily with oxygen are apt to combine with sulfur. With much less ease sulfur combines with many nonmetals such as chlorine and carbon.

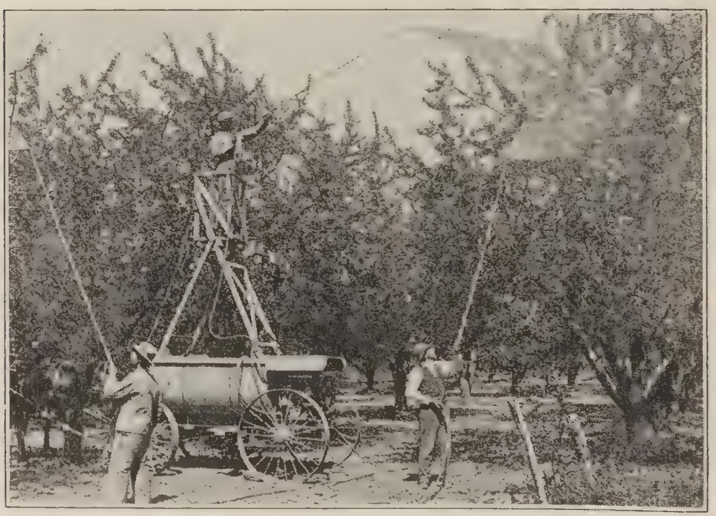


FIG. 150. Spraying an orchard of fruit trees with lime-sulfur spray

324. Uses of sulfur. Large quantities of sulfur are used in the manufacture of gunpowder, vulcanized rubber, sulfuric acid, and other compounds of the element. It is also used extensively in the manufacture of insecticides for use in orchards and vineyards.

325. Lime-sulfur spray. The chief sulfur insecticide is known as *lime-sulfur spray.* It is made by boiling sulfur with slaked lime, by which process a deep-red liquor is obtained, consisting essentially of a solution of sulfides of calcium (CaS_4 and CaS_5). The liquid is a very effective insecticide, particularly for scale, and it is also a fungicide. Large quantities of it are used for spraying fruit trees (Fig. 150). Flowers of sulfur is often used as a fungicide, not because it is poisonous but because with air and water it slowly produces poisonous compounds.

The Sulfides

326. Hydrogen sulfide (H_2S): properties. Sulfur forms with hydrogen the important compound known as hydrogen sulfide (H_2S). This is a colorless gas having a weak, disagreeable taste and a most offensive odor, suggesting rotten eggs, which, indeed, owe their odor to it. Under ordinary conditions (1 atmosphere and 20°) it is but sparingly soluble in water, 100 volumes of water dissolving 290 volumes of the gas; in boiling water it is not soluble at all. It is 1.18 times as heavy as air. When inhaled in concentrated form it acts as a violent poison, and even when much diluted with air it produces headache, dizziness, and nausea. Great caution must be exercised in working with it. Fortunately its odor gives warning of its presence.

327. Occurrence. Hydrogen sulfide is found in the vapors issuing from volcanoes. It also occurs in solution in many natural waters (*sulfur waters*). It is formed when organic matter containing sulfur undergoes decay, just as ammonia is formed from nitrogenous matter.

328. Preparation. Since hydrogen sulfide is a gas which is but little soluble in water, it can be prepared *by treating a sulfide with an acid* (Fig. 151). Iron sulfide (FeS) is usually employed:

$$FeS + 2\,HCl \longrightarrow FeCl_2 + \overline{H_2S}$$

329. Chemical conduct. The most important chemical properties of hydrogen sulfide are the following:

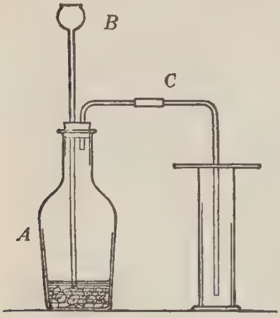


FIG. 151. Preparation of hydrogen sulfide

Iron sulfide is placed in flask *A* and hydrochloric acid is added through *B*. Hydrogen sulfide escapes through *C* and is collected by displacement of air

1. ***Acid properties.*** When dissolved in water, hydrogen sulfide acts as a *weak acid,* the solution being sometimes called *hydrosulfuric acid.* The solution turns blue litmus red and neutralizes bases, forming salts called *sulfides.*

2. ***Action with oxygen.*** The elements composing hydrogen sulfide have each a strong tendency to combine with oxygen and are not held together very firmly. Consequently the gas burns readily in oxygen or air according to the equation

$$2\,H_2S + 3\,O_2 \longrightarrow 2\,H_2O + 2\,SO_2$$

When there is not enough oxygen for both the sulfur and the hydrogen or when the temperature is kept low, the latter element combines with the oxygen, and the sulfur is set free:

$$2\,H_2S + O_2 \longrightarrow 2\,H_2O + 2\,S$$

It is probable that some of the sulfur in volcanic regions is produced by this reaction.

3. ***Reducing action.*** Owing to the ease with which hydrogen sulfide decomposes and the strong tendency of both sulfur and hydrogen to combine with oxygen, the substance is a strong *reducing* agent.

4. ***Action on metals.*** Hydrogen sulfide acts upon many metals, forming *sulfides.* Silver sulfide (Ag_2S) is black, and it is owing to traces of hydrogen sulfide in the air that silver objects tarnish.

330. Sulfur waters. The waters of many natural springs hold hydrogen sulfide in solution, as is indicated by their strong odor and the way in which they will blacken a silver coin. When the water reaches the air the hydrogen sulfide is slowly oxidized, with the liberation of sulfur, which often deposits about the borders of the spring.

331. Salts of hydrosulfuric acid; sulfides. The salts of hydrosulfuric acid (called *sulfides*) are an important class of compounds. Nearly all the heavier metals are found in nature chiefly as sulfides, and most of the sulfur of the world is combined with iron as iron disulfide (FeS_2). Most of the copper, lead, zinc, and silver of commerce is produced from mineral sulfides. As we have seen, lime-sulfur spray is largely composed of sulfides of calcium.

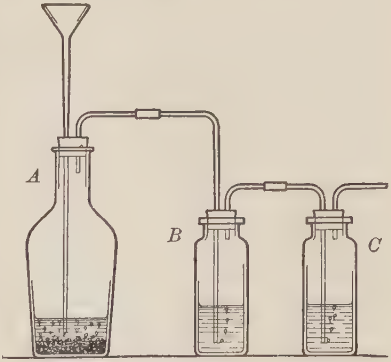


FIG. 152. Preparation of insoluble sulfides

Hydrogen sulfide is generated in flask *A* and passed into solutions of salts in bottles *B* and *C*

332. Uses of the sulfides in analysis. Most of the sulfides are insoluble in water, and some of them are insoluble in acids. Consequently, when hydrogen sulfide is bubbled through a solution of a salt it often happens that a sulfide is precipitated (Fig. 152). With copper chloride the equation is

$$CuCl_2 + H_2S \longrightarrow \underline{CuS} + 2\,HCl$$

Because of the fact that some metals are precipitated in this way as sulfides, while others are not, hydrogen sulfide is extensively used in the separation of the metals in the process of chemical analysis.

333. Test for the sulfide ion. Both hydrosulfuric acid and all soluble sulfides give sulfide ions, S^{--}, in solution. If we wish to test for the presence of this ion in a solution, we simply add to it the salt of some metal that forms an *insoluble* sulfide of characteristic color. A silver salt produces a *black* precipitate of silver sulfide (Ag_2S):

$$2\ AgNO_3 + H_2S \longrightarrow \underline{Ag_2S} + 2\ HNO_3$$

The black precipitate at once indicates the presence of S^{--} ions.

334. Carbon disulfide (CS_2). When sulfur vapor is passed over highly heated carbon, the two elements combine, forming *carbon disulfide* (CS_2), just as oxygen and carbon unite to form carbon dioxide (CO_2). The substance is a heavy, colorless liquid possessing a pleasant odor when pure. On standing, especially when exposed to sunlight, it undergoes a slight decomposition and acquires a most disagreeable odor. *It is a very good solvent for many substances, such as gums, rubber, waxes, and fats, which are insoluble in most liquids.* It boils at a low temperature (46°), and its vapor is not only very poisonous but very inflammable. It is prepared in considerable quantities for use as a solvent, as an insecticide, and in the manufacture of carbon chloride.

CHAPTER SUMMARY IN QUESTION FORM

1. Name the countries that have the largest deposits of sulfur.

2. (*a*) In what forms does sulfur occur in nature? (*b*) Is there any in our bodies?

3. (*a*) Why cannot the sulfur in the Texas and Louisiana deposits be mined like coal? (*b*) Who finally devised a way of obtaining this sulfur?

4. (*a*) In the process referred to in question 3, what two substances are used? (*b*) What is the use of each of these?

5. Name two common commercial varieties of sulfur.

6. Give the changes which sulfur undergoes when it is heated from room temperature to its boiling point.

7. (*a*) Name the three allotropic forms of sulfur, and (*b*) state how each can be formed. (*c*) Which is the most stable form?

8. (*a*) Name a liquid in which sulfur is soluble, and (*b*) give the form of sulfur that remains when the solution is evaporated.

9. What compound is formed when sulfur combines (*a*) with oxygen? (*b*) with a metal such as iron?

10. What is the importance of sulfur in connection (*a*) with the automobile industry? (*b*) with the raising of fruits?

11. Give in regard to the preparation of hydrogen sulfide (*a*) the name of the compounds used; (*b*) the products of the reaction; (*c*) the equation for the reaction; (*d*) the method of collecting it.

12. Supply the missing words in the following: Hydrogen sulfide is a ______ and has a ______ odor. When inhaled it is ______. It is ______ soluble in ______. The solution turns blue litmus red, and is therefore an ______. This solution is called ______ acid, and its salts are called ______.

13. Hydrogen sulfide burns when ignited in air. Write the equation for its combustion (*a*) when there is plenty of air; (*b*) when the supply of air is limited.

14. (*a*) What compounds give the sulfide ion, S^{--}, in solution? (*b*) How can you test a solution for the presence of this ion?

15. Supply the missing words in the following: Just as carbon unites with oxygen to form ______ ______, so it unites with sulfur to form ______ ______. This is a heavy ______, of very ______ odor. Its two chief uses are as a ______ and as an ______.

THOUGHT QUESTIONS

1. Iron sulfide (FeS_2) is a mineral called "fool's gold" because it looks like gold. How could you tell it from gold?

2. (*a*) Name the elements so far studied that occur in allotropic forms. (*b*) Give the names of the different forms.

3. Suppose you were to grind a part of a stick of sulfur to a fine powder. Would the powder and the stick be allotropic forms of sulfur?

4. How could you tell whether any two forms of an element are allotropic forms of the element or simply different physical states of the same form?

5. The reaction used in the preparation of hydrogen sulfide is a reversible one. Why does it complete itself?

6. Hydrogen sulfide is as poisonous as carbon monoxide, yet we do not fear it as we do carbon monoxide. Why?

7. We often hear of "sulfur waters" and "sulfur springs"; yet sulfur is insoluble in water. Explain.

8. When ignited, carbon disulfide burns in air, both of the elements present being completely oxidized. Write the equation for the reaction.

FOR HONOR STUDENTS

1. Calculate (*a*) the number of liters of oxygen required to burn 10 liters of hydrogen sulfide, and (*b*) the number of liters of sulfur dioxide formed.

2. Consult the table of solubilities (Appendix D) and note sulfides that are soluble in water. Predict what will happen when hydrogen sulfide is passed into solutions of each of the following compounds, writing the equations for any reactions that may occur, and underscoring compounds that are precipitated: (*a*) silver nitrate ($AgNO_3$); (*b*) copper sulfate ($CuSO_4$); (*c*) sodium chloride; (*d*) potassium hydroxide; (*e*) lead nitrate ($Pb(NO_3)_2$).

3. Prepare a table giving the following information concerning the elements we have so far studied:

NAME OF ELEMENT	PHYSICAL STATE	COLOR	ODOR	SOLUBILITY IN WATER	WILL IT BURN?

CHAPTER XXIV

THE OXIDES OF SULFUR AND THEIR ACIDS

Two Compounds with Very Important Near Relatives

335. ***Introduction.*** Sulfur forms two well-known compounds with oxygen: sulfur dioxide (SO_2) and sulfur trioxide (SO_3). As we shall see, these are very important compounds, both because of their own properties and, more largely, because of the compounds they form. They are both *acid anhydrides* (§ 305), combining with water to form *sulfurous acid* and *sulfuric acid*, both of which are of the greatest importance in chemical industries.

I. Sulfur Dioxide — Sulfurous Acid

336. Sulfur dioxide (sulfurous anhydride) (SO_2). Sulfur dioxide is a colorless gas which at ordinary temperatures is 2.2 times as heavy as air. It has a peculiar, irritating odor. It is very soluble in water, 1 volume of water at ordinary temperature dissolving about 80 volumes of the gas. At ordinary temperature it can be liquefied to a colorless liquid by a pressure of about 3 atmospheres. Under atmospheric pressure this liquid boils at – 10°. Liquid sulfur dioxide is often shipped in tank cars like gasoline (Fig. 153).

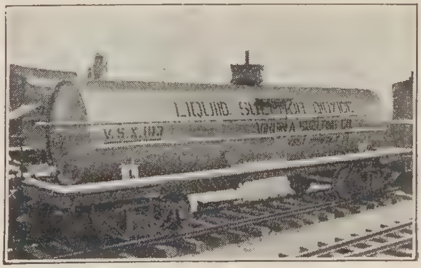


FIG. 153. Tank car of liquid sulfur dioxide

337. Occurrence. Sulfur dioxide often occurs in nature in the gases issuing from volcanoes, and in solution in the water of many springs. It is likely to be found wherever sulfur compounds are undergoing oxidation.

338. Preparation. Two general ways may be mentioned for the preparation of sulfur dioxide:

1. ***By the combustion of sulfur.*** Sulfur dioxide is readily formed when sulfur or certain compounds containing sulfur, such as the metal sulfides, are heated in air or oxygen:

$$S + O_2 \longrightarrow SO_2$$
$$2\ ZnS + 3\ O_2 \longrightarrow 2\ ZnO + 2\ SO_2$$

Coal almost always contains sulfur, and we notice the irritating odor of sulfur dioxide about inclosed railway stations.

2. ***By the reduction of sulfuric acid.*** When concentrated sulfuric acid is heated with certain metals, such as copper, part of the acid is changed into copper sulfate and part is reduced to sulfurous acid, the latter decomposing into sulfur dioxide and water. The details of the reaction will be given later, but the complete equation is as follows:

$$Cu + 2\ H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2\ H_2O$$

339. Chemical conduct. Sulfur dioxide has a marked tendency to combine with other substances and is therefore an active substance chemically. It combines with oxygen gas, but not very easily. It can, however, take oxygen away from some other substances and is therefore a good reducing agent. Its most marked chemical property is its ability to combine with water.

340. Uses. The most important uses of sulfur dioxide are in the preparation of sulfurous acid and its salts and of sulfuric acid, and as a refrigerating agent.

The use of liquid ammonia in cold-storage rooms and for freezing ice has already been explained (Figs. 136, 137), and liquid sulfur dioxide is very widely used in exactly the same way. It absorbs only about one third as much heat on evaporation as does liquid ammonia, but it requires very much less pressure to liquefy it (less than half as much at room temperature). Consequently it is best adapted to domestic refrigerators (Fig. 154) operated by a small compression pump, while ammonia is used in large units. Both ammonia and sulfur dioxide have marked odors, so that leaks in the pipes are easily detected.

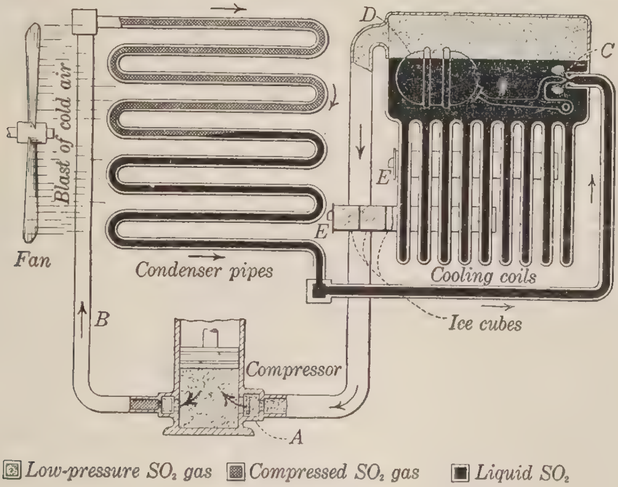


FIG. 154. Diagram to show how the electric household refrigerator operates

Gaseous sulfur dioxide enters the compressor at *A*. The compressed gas is forced upward through the pipe *B*, is cooled by the fan, and liquefies in the condenser pipes. The liquid then enters the icebox at *C*, where it evaporates, cooling the liquid in the coils to a low temperature. The evaporated gas returns to the compressor. The float-valve *D* regulates the circulation of the liquid sulfur dioxide

341. Sulfurous acid (H_2SO_3). When sulfur dioxide is passed into water it combines chemically with it to form *sulfurous acid* (H_2SO_3). It is impossible to prepare this acid in pure form, as it breaks down very easily into water and sulfur dioxide. The reaction is therefore reversible and is expressed by the equation

$$H_2O + SO_2 \rightleftarrows H_2SO_3$$

Solutions of the acid in water are often prepared and have a number of interesting properties and commercial uses.

1. ***Acid properties.*** The solution has all the properties of a very weak acid. When neutralized by bases, sulfurous acid yields salts called *sulfites,* most of which are insoluble in water.

2. ***Reducing properties.*** Solutions of sulfurous acid act as good reducing agents. This is due to the fact that sulfurous acid has the power of taking up oxygen from the air, or from substances in which oxygen is held rather loosely, and is changed by this reaction into sulfuric acid:

$$2\ H_2SO_3 + O_2 \longrightarrow 2\ H_2SO_4$$

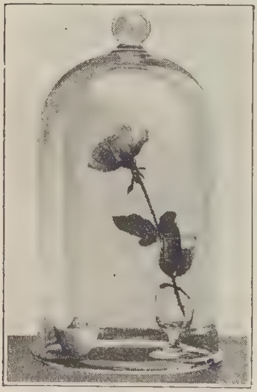


FIG. 155. Bleaching of a moist flower with fumes of burning sulfur

3. ***Bleaching properties.*** Sulfurous acid has bleaching properties, although it is not as good a bleaching agent as chlorine (§ 215, 2). It is used, however, to bleach substances that would be injured by the action of chlorine, such as paper, silk, straw goods, feathers, and even such foods as canned corn and dried fruits. Bleaching is often accomplished by merely exposing the *wet* material to the fumes of burning sulfur (Fig. 155). As a rule the bleaching is not permanent, the color returning with exposure to air and sunshine, as in the case of a straw hat that has been bleached.

4. ***Toxic action.*** Sulfurous acid is strongly poisonous to vegetable organisms. Vegetation is rapidly killed near smelters that liberate sulfur dioxide.

342. Salts of sulfurous acid; sulfites. The sulfites are solid compounds. Like sulfurous acid, they have the power of taking up oxygen very readily and are good reducing agents as well as bleaching agents. On account of this tendency commercial sulfites are often contaminated with sulfates. Calcium sulfite is used in great quantities in the manufacture of paper from wood, since it dissolves the gluelike material and leaves the pure cellulose (paper material).

II. Sulfur Trioxide — Sulfuric Acid

343. Sulfur trioxide (sulfuric anhydride) (SO_3). Sulfur trioxide is a colorless liquid which solidifies at about 15° and boils at 46°. A trace of moisture causes it to solidify into a mass of silky white crystals which have the formula S_2O_6. In contact with the air it fumes strongly, and when thrown upon water it dissolves with a hissing sound and the liberation of a great deal of heat. The product of this reaction is sulfuric acid, so that sulfur trioxide is the *anhydride* of that acid (§ 305):

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

344. Preparation. When sulfur dioxide and oxygen are heated together at a rather high temperature, a small amount of sulfur trioxide (SO_3) is formed, but the reaction is slow and incomplete. If, however, a suitable catalytic agent (finely divided platinum) is present (Fig. 156), the reaction is rapid and nearly complete:

$$2\,SO_2 + O_2 \longrightarrow 2\,SO_3$$

345. Sulfuric acid (oil of vitriol) (H_2SO_4). Strictly speaking, sulfuric acid is a solution of hydrogen sulfate (H_2SO_4) in water. It is customary, however, to call both hydrogen sulfate and also its aqueous solution by the name *sulfuric acid.* The pure compound is a colorless oily liquid nearly twice as heavy as water. The ordinary concentrated acid of commerce contains about 2 per cent of water, has a density of 1.84, and boils at 338°. It is sometimes called *oil of vitriol.*

Sulfuric acid is one of the most important of all manufactured chemicals and is rightly called the "king of chemicals." Next to water, it is the liquid most used in chemical industries. Enormous quantities are used in many of the industries, especially in dissolving off the oxidized scale from metals, in the refining of petroleum, and in the manufacture of explosives, dyes, hydrochloric and nitric acids, and phosphate fertilizers. It is one of the most used laboratory reagents.

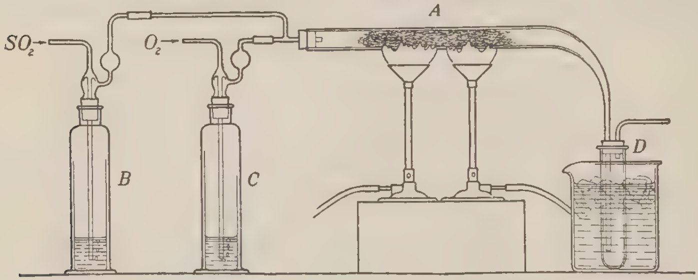


FIG. 156. The preparation of sulfur trioxide

Sulfur dioxide and oxygen, dried by bubbling through concentrated sulfuric acid in *B* and *C*, are together passed over the heated catalyst *A*. Sulfur trioxide condenses in *D*

346. Manufacture of sulfuric acid. Sulfuric acid can be made at low cost and is the cheapest of the commercial acids, since other acids are so largely made by using it. Two general methods are used in its manufacture:

1. ***Contact process.*** In this process sulfur trioxide is first made from sulfur dioxide and oxygen by the use of a catalyst as explained under Fig. 156. In this country the sulfur dioxide is obtained by burning sulfur. Platinum has usually been employed as the catalyst, but compounds of the element *vanadium* are being employed in all new plants.

The sulfur trioxide so obtained reacts with water to form sulfuric acid:

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

The contact process produces *concentrated* acid (Fig. 157), and this is the kind demanded by nearly all industries requiring sulfuric acid, save in the manufacture of fertilizers. Even in industries using dilute acid it is often cheaper to buy concentrated acid than to pay freight on the water present in the dilute acid.

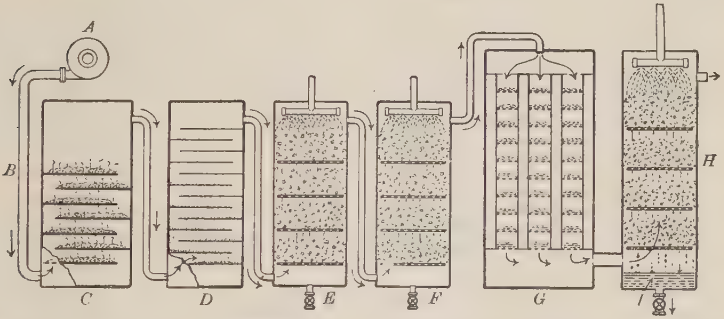


FIG. 157. Diagram to illustrate the commercial preparation of sulfuric acid by the contact process

The sulfur in the chamber *C* is burned by the air forced into the chamber by the blower *A*. The resulting sulfur dioxide and oxygen (air) are freed from dust by passing through the chambers *D* and *E* and dried by a spray of sulfuric acid in *F*. The gases are then passed over the catalyst in *G*, where sulfur trioxide is formed by the union of the sulfur dioxide and oxygen. The resulting sulfur trioxide is absorbed in the chamber *H*, by means of concentrated sulfuric acid, and the resulting product drawn off at *I*

2. ***Chamber process.*** The older method of manufacture, exclusively employed until comparatively recent years and still of great importance, is much more complicated. The conversion of water, sulfur dioxide, and oxygen into sulfuric acid is accomplished by the catalytic action of oxides of nitrogen. These are obtained by the catalytic oxidation of ammonia (§ 294). Since these oxides are gases, it is difficult to prevent their escape; and very elaborate precautions

have to be taken to reduce the loss as much as possible. The reactions are brought about in very large lead chambers into which oxides of nitrogen, sulfur dioxide, steam, and air (to furnish oxygen) are introduced in suitable proportions.

The dilute acid which collects upon the floor of the lead chambers contains from 62 to 70 per cent of hydrogen sulfate. It is drawn off and in this form serves for many purposes, such as the manufacture of fertilizers. The pure concentrated acid can be prepared from the dilute acid by evaporation of the water, but the process is costly, so that it is usually cheaper to prepare this form of acid by the contact process.

347. Chemical conduct. Sulfuric acid possesses properties which make it one of the most important of chemical substances.

1. ***Action as an acid.*** In dilute solution sulfuric acid acts as a very strong acid, turning blue litmus red, forming salts with oxides and hydroxides, and in general having all the properties characteristic of acids.

2. ***Action as an oxidizing agent.*** Sulfuric acid contains a large percentage of oxygen and, like nitric acid, is rather easily decomposed. Consequently it is a very good oxidizing agent. When the concentrated acid is heated with sulfur or carbon or various other substances, oxidation takes place, the sulfuric acid decomposing according to the equation

$$2\,H_2SO_4 \longrightarrow 2\,H_2O + 2\,SO_2 + O_2$$

A great quantity of concentrated sulfuric acid is used as an oxidizing agent in manufacturing dyes, the sulfur dioxide formed being converted once more into sulfuric acid by the contact method.

3. ***Action on metals.*** *Dilute* sulfuric acid acts on the metals above hydrogen in the electrochemical series, forming salts of the acid (*sulfates*) and liberating hydrogen (§ 256). The *concentrated* acid, being a good oxidizing agent, acts in

a different way upon the metals above hydrogen in the displacement series, as well as upon most of the metals below hydrogen. The metal is first oxidized by the acid; the resulting oxide then reacts with more of the acid, forming a salt and water. Thus, with copper the equations are

$$Cu + H_2SO_4 \longrightarrow CuO + H_2O + SO_2 \qquad (1)$$
$$CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O \qquad (2)$$

By canceling the formula of copper oxide in these equations (since the oxide produced in the first reaction is used up in the second) we may combine the two equations into a single one; namely,

$$Cu + 2\ H_2SO_4 \longrightarrow CuSO_4 + 2\ H_2O + SO_2$$

This equation tells us what materials are used up and what the final products are; it does not tell us what materials may have been produced and consumed in the process.

4. ***Action on salts.*** We have repeatedly seen that an acid of high boiling point heated with the salt of some acid of lower boiling point will drive out the low-boiling acid (§ 314, 1). The boiling point of sulfuric acid (338°) *is higher than that of almost any other common acid*; hence it is largely used in the preparation of other acids. For example, the equation for the preparation of *nitric acid* is

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$$

5. ***Action on water.*** Concentrated sulfuric acid has a very great affinity for water and is therefore an effective drying, or *dehydrating*, agent. Gases which have no chemical action upon sulfuric acid can be freed from water vapor by bubbling them through the concentrated acid.

Not only can sulfuric acid absorb water, but it will often withdraw the elements hydrogen and oxygen from a compound containing them, decomposing the compound and combining with the water so formed. For this reason most organic substances, such as sugar, wood, cotton and woolen fiber, and even flesh, all of which contain much oxygen and hydrogen in addition to carbon, are charred by the action of the concentrated acid.

348. Salts of sulfuric acid; sulfates. The sulfates form a very important class of salts, and many of them have commercial uses. *Copperas* (iron sulfate), *blue vitriol* (copper sulfate), and *Epsom salt* (magnesium sulfate) serve as examples. Many sulfates are important minerals, prominent among these being *gypsum* (calcium sulfate) and *barite* (barium sulfate).

349. Test for sulfate ions, SO_4^{--}. Nearly all the sulfates are soluble in water and are freely ionized, as is sulfuric acid, producing sulfate ions, SO_4^{--}. Barium sulfate ($BaSO_4$) is one of the few sulfates *insoluble both in water and in acids* (the others being the sulfates of lead and strontium). Consequently when a solution of a soluble barium salt (barium chloride, $BaCl_2$) is added to a solution containing SO_4^{--} ions and hydrochloric acid, a *white precipitate* at once forms:

$$Ba^{++}, Cl^-, Cl^- + H^+, H^+, SO_4^{--} \longrightarrow \underline{BaSO_4} + 2(H^+, Cl^-)$$

This reaction constitutes a delicate test for SO_4^{--} ions. There are other barium salts insoluble *in water*, but no others insoluble in *acids*; so hydrochloric acid must be added in making the test.

350. Monobasic and dibasic acids. Acids like hydrochloric and nitric acids, which have only *one* replaceable hydrogen atom in the molecule (or, in other words, which yield one hydrogen ion in solution), are called *monobasic* acids. Acids like sulfuric acid, which have *two* replaceable hydrogen atoms in each molecule, are called *dibasic* acids. Similarly, we may have *tribasic* and *tetrabasic* acids.

351. Normal and acid salts. It is possible for such acids as H_2S, H_2SO_3, and H_2SO_4 to form two kinds of salts. In the one both of the hydrogen atoms of the acid have been replaced by atoms of a metal, as in the salts Na_2S and Na_2SO_4. These are called *normal salts.* In the other only one of the hydrogen atoms has been replaced, as in the salts NaHS and $NaHSO_4$. These are called *acid salts,* since in solution they give the ions both of a salt and of an acid. Acid salts are often designated by the prefix *bi-*; thus, $NaHSO_4$ is called sodium bisulfate. It is also called sodium acid sulfate, or sodium hydrogen sulfate.

CHAPTER SUMMARY IN QUESTION FORM

1. Give the formulas and names of two important oxides of sulfur.

2. In the laboratory preparation of sulfur dioxide, (*a*) what substances are used? (*b*) Name the compounds formed. (*c*) Write the equation for the reaction.

3. Give four physical properties of sulfur dioxide.

4. Which is the easiest to liquefy: oxygen, helium, or sulfur dioxide?

5. Supply the missing words in the following: When sulfur dioxide is passed into water, part of the gas ------ and part unites with the water, forming ------ ------, which turns ------ litmus ------; its salts are called ------.

6. Give three important uses of sulfur dioxide.

7. (*a*) What properties of sulfur dioxide are taken advantage of in the freezing of water in household electric refrigerators? (*b*) Explain the action of such refrigerators.

8. Supply the missing words in the following, which refers to the preparation of sulfuric acid: ------ burns in air to form ------ ------, which is then mixed with air, purified, and passed over a hot, finely divided catalyst to form ------ ------. This is dissolved in ------ to form ------ ------. This method of preparation is known as the ------ process.

9. (*a*) Name an acid and a base that are used on an enormous scale in all civilized countries. (*b*) Name a few of the uses of each.

10. Zinc dissolves in dilute sulfuric acid. Name the substances formed.

11. Copper dissolves in concentrated sulfuric acid. Name the compounds formed.

12. Sulfuric acid acts on sodium nitrate. Name the two compounds formed.

13. (*a*) What name is given to the salts of sulfuric acid? (*b*) Give the names and formulas for the salts of sulfuric acid that are insoluble (see table of solubilities in Appendix D).

14. (*a*) What compounds in water solution give the SO_4^{--} ion? (*b*) Give the test for this ion.

15. Classify each of the following acids as monobasic, dibasic, or tribasic; also each of the salts as a normal or acid salt: HCl, KCl, H_2SO_4, $Ca(NO_3)_2$, H_2CO_3, $NaHCO_3$, H_3PO_4, Na_2HPO_4, H_2S, Ag_2S, $NaHS$.

THOUGHT QUESTIONS

1. (*a*) Name three compounds studied that act as bleaching agents. (*b*) Name the conduct of each that gives it the power of bleaching.

2. In what ways do sulfur dioxide and carbon dioxide resemble each other?

3. Write the equation for the reaction that takes place when sulfuric acid is added (*a*) to Na_2CO_3; (*b*) to Na_2SO_3.

4. (*a*) Do the reactions in question 3 go to completion? (*b*) If so, why?

5. (*a*) Compare the reactions of nitric acid and of concentrated sulfuric acid on copper. (*b*) How do these reactions resemble each other?

6. Suggest a test for sulfites (not an ion test). (Recall that sulfur dioxide has a characteristic odor.)

7. Nitric acid is prepared by the action of sulfuric acid on sodium nitrate. Is the sulfuric acid used because it is a strong acid, because it has a high boiling point, because it is a liquid, or because it is a very cheap acid?

8. Do you think you could prepare nitric acid by treating sodium nitrate with hydrochloric acid?

9. State (*a*) the names and formulas of the three important acids studied; (*b*) their action on bases; (*c*) which can act as oxidizing agents; (*d*) which is a dehydrating agent.

10. In burning sulfur what relation exists between the volume of oxygen required and the volume of sulfur dioxide formed?

11. Calculate the percentage of oxygen in each of the oxides of sulfur.

FOR HONOR STUDENTS

1. Enumerate the reactions so far studied in which catalysts have been employed.

2. Read Chapter XII in Foster's "The Romance of Chemistry" (entitled "Sulfur, a Pillar of Industry"), and write a brief theme on the subject.

3. Assuming that none was lost in the process, what weight of sulfur would be required daily in a plant that produced 1000 tons of sulfuric acid daily?

CHAPTER XXV

THE PERIODIC LAW

Family Groups of Similar Elements

352. ***Introduction.*** The practical gardener must know a little about a great many varieties of plants. Instead of trying to learn all about each variety separately, he saves time and effort by arranging them in groups for his convenience. One group will grow best in abundant sunshine, another in shady places; one group needs plenty of water, another will stand dry weather well; one flourishes best in a clay soil, another requires a sandy loam. This is merely a *practical* classification, and brings together plants of very different kinds in the same group.

The scientific botanist feels that there is a much more fundamental basis for classification. He thinks of plants as *related* to each other — as brothers and sisters, as cousins, as distant relatives — and he tries to trace out these relationships. He seeks a *natural* classification.

353. Classification of the elements. The earlier chemists classified the elements much as a gardener classifies plants, having in mind only convenience and practical use. They grouped them as metals and nonmetals; as heavy elements, light elements, and gaseous elements; as acid-forming elements and base-forming elements.

As the number of known elements increased and more was learned about them, chemists were convinced that natural relations exist between elements just as they do between plants. They felt sure that if this relationship could be discovered, and the elements should be arranged

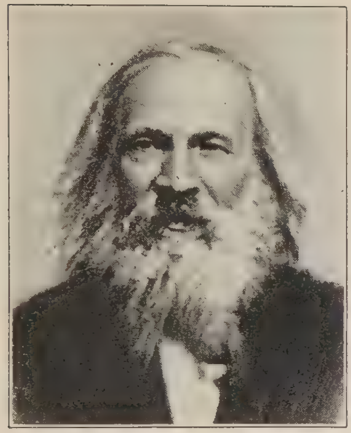


FIG. 158. D. I. Mendeléeff
(1834–1907)

A Russian chemist who is noted chiefly for proposing the periodic classification of the elements

FIG. 159. H. G. J. Moseley
(1888–1915)

The English physicist who proved that the properties of an atom depend upon its atomic number

FIG. 160. J. J. Thomson
(1856–)

FIG. 161. F. W. Aston
(1877–)

Two English physicists who proved that many of the elements are mixtures of isotopes

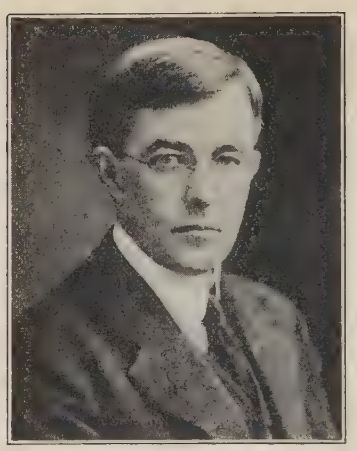


FIG. 162. I. Langmuir (1881-   )

FIG. 163. G. N. Lewis (1875-   )

Two American chemists who have contributed to our knowledge of the periodic law and the structure of the atom

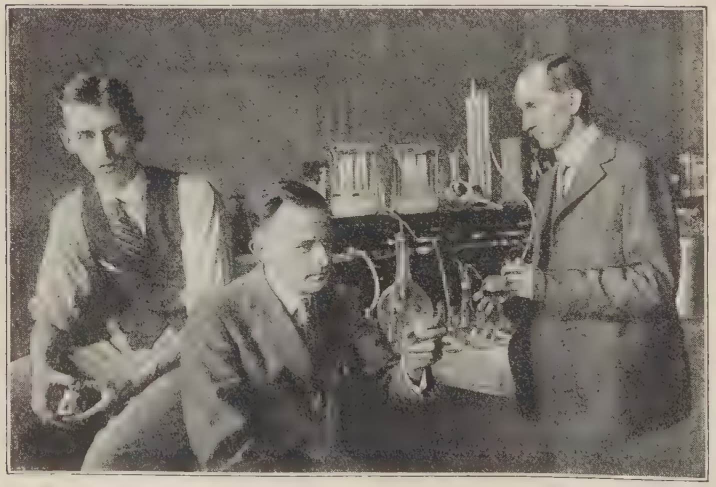


FIG. 164. Dr. Hopkins (at the right) with his associates at the University of Illinois at work on illinium, the only element ever discovered by an American

Material rich in illinium is contained in the small vessel held by the central worker in *natural* groups or families, the study of chemistry would be much simplified and the discovery of many new facts would result.

Many ingenious and interesting plans for classifying the elements were proposed from time to time, and finally in 1869 the Russian chemist Mendeléeff (Fig. 158) discovered a natural relationship known as the *periodic law*. Since about 1914 the classification of elements according to the periodic law has rested upon the *atomic number* of each element (§ 193).

354. Atomic number. In 1913–1914 the young English physicist Moseley (Fig. 159), killed early in the World War, devised a remarkable method for measuring directly the nuclear charge of the various kinds of atoms. It will be remembered that the nuclear charge of an atom is the excess of the positive charges (protons) over the negative charges (electrons) comprising the *nucleus* of the atom (§ 193). (This excess number is also equal to the number of *satellite* electrons belonging to the atom.) Moseley's method was a purely physical one, depending upon measurements of X-ray spectrum lines of the elements, and need not be described here.

From the results of these experiments Moseley was able to arrange the elements in a numbered order in a row. Hydrogen is number 1 (nuclear charge 1), helium is number 2 (nuclear charge 2), lithium is number 3 (nuclear charge 3), and so on up to uranium, number 92 (nuclear charge 92). Each element has its atomic number, which can be determined by experiment.

355. The periodic grouping. Now we can arrange the various elements *in the order of their atomic numbers* in a way that brings to light most interesting relationships. Omitting hydrogen, which has the smallest atomic number (1), and beginning with helium, of atomic number 2, the succeeding seven elements are arranged in a horizontal row *in the order of their atomic numbers,* as in the first line of the table, p. 289. These eight elements differ markedly from each other in chemical behavior, but neon, of atomic number 10, is very similar to helium. It is placed just below helium, and a new horizontal row follows, as shown below. The element following chlorine — namely, argon — resembles helium and neon and begins a third row:

He (2)	Li (3)	Be (4)	B (5)	C (6)	N (7)	O (8)	F (9)
Ne (10)	Na (11)	Mg (12)	Al (13)	Si (14)	P (15)	S (16)	Cl (17)
A (18)	K (19)	Ca (20)	Sc (21)	Ti (22)	V (23)	Cr (24)	Mn (25)

If we now notice the elements that fall in *vertical* columns in these three rows, a remarkable fact comes to light. Not only is there a strong similarity between helium, neon, and argon, which form the first vertical column, *but the elements in each of the other columns have the same kind of similarity among themselves and evidently form natural groups.* Thus lithium, sodium, and potassium form a group of similar elements, as do also beryllium, magnesium, and calcium.

Iron, cobalt, and nickel, following manganese, have atomic weights much nearer together than do any of the elements of smaller atomic number; they resemble each other strongly, but are not like any of the elements so far considered. So they are placed in a ninth column by themselves.

The first three horizontal rows of the table (p. 289) show the arrangement of these twenty-seven elements. A new row is begun with copper. Following the fifth and seventh rows are sets of three closely related elements placed under iron, cobalt, and nickel in the ninth column. The complete arrangement is given in the table.

356. Properties of elements and their atomic numbers. When we compare the elements in the first horizontal row with each other, we find that their properties change in an interesting way as the atomic number increases. Helium combines with no other element and therefore has no

THE PERIODIC ARRANGEMENT OF THE ELEMENTS ACCORDING TO ATOMIC NUMBERS

Type of hydride		RH	RH_2	RH_3	RH_4	RH_3	RH_2	RH			
Type of oxide		R_2O	RO	R_2O_3	RO_2	R_2O_5	RO_3	R_2O_7	RO_4		
SERIES	GROUP 0	GROUP I	GROUP II	GROUP III	GROUP IV	GROUP V	GROUP VI	GROUP VII	GROUP VIII		
1	2 He = 4.002	3 Li = 6.94	4 Be = 9.02	5 B = 10.82	6 C = 12.00	7 N = 14.008	8 O = 16.000	9 F = 19.00			
2	10 Ne = 20.188	11 Na = 22.997	12 Mg = 24.32	13 Al = 26.97	14 Si = 28.06	15 P = 31.02	16 S = 32.06	17 Cl = 35.457			
3	18 A = 39.94	A B 19 K = 39.10	A B 20 Ca = 40.07	A B 21 Sc = 45.10	A B 22 Ti = 47.90	A B 23 V = 50.96	A B 24 Cr = 52.01	A B 25 Mn = 54.93	26 Fe = 55.84	27 Co = 58.94	28 Ni = 58.69
4		29 Cu = 63.57	30 Zn = 65.38	31 Ga = 69.72	32 Ge = 72.60	33 As = 74.93	34 Se = 79.2	35 Br = 79.916			
5	36 Kr = 82.9	37 Rb = 85.44	38 Sr = 87.63	39 Y = 88.92	40 Zr = 91.22	41 Cb = 93.1	42 Mo = 96.0	43 Ma = (?)	44 Ru = 101.7	45 Rh = 102.91	46 Pd = 106.7
6		47 Ag = 107.88	48 Cd = 112.41	49 In = 114.8	50 Sn = 118.70	51 Sb = 121.77	52 Te = 127.5	53 I = 126.932			
7	54 Xe = 130.2	55 Cs = 132.81	56 Ba = 137.36	57 La = 138.90 *	72 Hf = 178.6	73 Ta = 181.5	74 W = 184.0	75 Re = 188.7	76 Os = 190.8	77 Ir = 193.1	78 Pt = 195.23
8		79 Au = 197.2	80 Hg = 200.61	81 Tl = 204.39	82 Pb = 207.22	83 Bi = 209.00	84 Po = 210 (?)	85 (†)			
9	86 Rn = 222	87 (†)	88 Ra = 225.97	89 Ac = 230 (?)	90 Th = 232.12	91 Pa = (?)	92 U = 238.14				

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* Following lanthanum occurs a series of elements, known as the rare earth elements, of atomic numbers 58–71. They all closely resemble lanthanum and so cannot be distributed among the several groups. † The discovery of numbers 85 and 87 has been announced but lacks confirmation.

chemical properties. We say it is an *inert* element. Following it, lithium is a metallic element, has a valence of 1, and is strongly base-forming. The next element, beryllium, has a valence of 2, and is less strongly base-forming; boron, with a valence of 3, has some base-forming and some acid-forming properties. In carbon, with a valence of 4, all base-forming properties have disappeared, and the acid-forming properties are more marked than in boron. These become still more emphasized as we pass through nitrogen and oxygen, and on reaching fluorine we have one of the strongest acid-forming elements. *The properties of these eight elements vary regularly with their atomic numbers*; or, in mathematical language, *their properties are regular functions of their atomic numbers.*

357. Properties of elements repeated. If it were true that helium had the smallest atomic number of any of the elements and fluorine the largest, so that in passing from one to the other we should include all the elements, we could say that the properties of all the elements are *regular functions* of their atomic numbers.

But fluorine is an element of relatively small atomic number, and the one following it, neon, breaks the order, *for in it reappear all the characteristic properties of helium.* Sodium, following neon, bears much the same relation to lithium that neon does to helium, and in general the properties of the elements in the second row vary in the same way as do the properties of the elements in the first row, until argon is reached. Then another repetition begins, argon being similar to helium and neon.

358. The periodic law. The properties of the elements do not vary in a *steady progression* with the atomic number, but at regular intervals there is a *repetition,* or *period.* This generalization is called the *periodic law,* which may be stated thus: *The properties of elements are periodic functions of their atomic numbers.*

359. Two families in a group. After the second row across the table (p. 289), the elements of each group (excepting Group 0) fall naturally into two subdivisions called *families*. The elements of each group in the *odd-numbered* horizontal rows form one family, those in the *even-numbered* rows the other. In the table these families are arranged under the headings *A* and *B*. The elements in family *A* in a group resemble one another much more closely than they resemble those in family *B* in the same group. Thus zinc, cadmium, and mercury form one family of very similar elements in Group II, while calcium, strontium, barium, and radium form the other.

The first two elements in each group (belonging to the first two horizontal rows) resemble one of the families (*A* or *B*) much more closely than the other. Thus, in Group I lithium and sodium resemble potassium, rubidium, and cesium rather than copper, silver, and gold; in Group VII fluorine and chlorine resemble bromine and iodine rather than manganese and the other elements in family *A*.

360. Family resemblances. What do we mean by saying that the elements in a family resemble each other?

1. ***Valence.*** In general the valence (or valences) of the elements in a family is the same, and the formulas of their compounds are therefore similar. The formulas R_2O, RO etc. placed above the group columns represent the usual oxides of the elements in each column, while the formulas RH, RH_2 etc. represent the hydrides or chlorides. In either case the letter R stands for the symbol of any one of the elements in either family.

2. ***Chemical conduct.*** The members of a family resemble each other in their chemical action. If one is a metal, the others usually are; if one is a nonmetal, so too are the others. There is also a somewhat regular gradation in the conduct of the elements in each family. If the top element is strongly acid-forming, as is nitrogen, the succeeding ones

are less so, and the lowest one may even have some metallic properties, as is true with bismuth (Group V). The intermediate elements are midway between the top and the bottom in their chemical nature.

3. ***Physical properties.*** In the same way, the physical properties of the members of a family are in general somewhat similar, and show a regular gradation as we pass from element to element in the family. Thus, the melting point, boiling point, density, and electrical conductance usually vary more or less regularly from element to element.

361. Value of the periodic law. The periodic law has been of the greatest service in the development of the science of chemistry.

1. ***It simplifies study.*** It is easy to see that the regularities brought to light among the elements simplify the study of chemistry. A thorough study of one element of a family makes a study of the others a much easier task.

2. ***It indicates probable error.*** When the periodic law was first announced, the physical constants of many of the elements, as then measured, did not agree with those required by the law. For example, many atomic weights were wrong. A further study of most of these cases showed that errors of measurement had been made, and these were speedily corrected.

3. ***It suggests the probable existence of new elements.*** When the periodic law was first announced, there were a number of vacant places in the table which evidently belonged to elements not yet discovered. From their position in the table it was possible to predict the properties of these missing elements, and even the kind of ores in which they would probably occur. As these elements were discovered, their properties were found to agree in a remarkable way with those predicted for them.

The atomic numbers of the elements range from 1 to 92, and of the ninety-two elements predicted, all are known with certainty except numbers 85 and 87. The discovery of these two has been announced recently by different scientists, and while the results seem convincing, it is probable that they will need further confirmation before they are generally accepted.

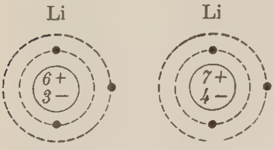
362. Imperfections of the periodic law. Like most scientific laws, the periodic law has its imperfections and limitations, which shows that we have not yet got at all the facts.

There is no place in the table for the very important element hydrogen. There is a group of elements, of atomic numbers 58 to 71, all of which resemble each other very closely and so cannot be distributed among the several groups. They are simply left out of the usual forms of the table. The similarities between elements in a family are merely *general,* not *exact.* We are never *certain* that an element will behave as its position predicts until we try it. It usually acts approximately as we should expect but not exactly so.

363. Can atoms of the same element have different weights? Up to this point we have assumed that all the atoms of a given element are exactly alike both in weight and in structure. Is this necessarily so?

In Chapter XIV we found (1) that the *weight* of an atom depends almost entirely on the weight of the protons in its nucleus; (2) that the *chemical properties* of an atom depend on the outer system of its valence electrons; and in this chapter we have learned (3) that the position of an element in the periodic table depends on the (positive) nuclear charge. If we could have two atoms with the same nuclear charge and the same number of valence electrons, *but with different nuclear weights,* we should have two atoms of the same chemical properties and therefore indistinguishable from each other, but with different weights. In other words, we should have two atoms of the *same element* with different atomic weights.

364. Isotopes. Two brilliant physicists, J. J. Thomson (Fig. 160) and F. W. Aston (Fig. 161), have proved that many elements do actually have atoms of several different weights. Fig. 165 represents the two different atoms of lithium. Each has a nuclear charge of 3 (+), and each has 1 valence electron. They are therefore atoms of the same element. But one has a weight of 6 (6 protons), while the other has a weight of 7. Two or more atoms of the same element but with different weights are called *isotopes* of that element.



A.N. 3 A.N. 3

FIG. 165. The isotopes of lithium

365. Fractional atomic weights. Since the weight of an atom is really the weight of its nucleus, and since the nucleus always consists of a definite number of protons (all of equal weight), *the weights of all atoms should be whole numbers* (§ 205). Yet many elements have fractional atomic weights, as, for example, chlorine, with the atomic weight 35.457. The reason for this is now clear. All elements that have fractional atomic weights have been shown to be mixtures of two or more isotopes, and each individual isotope has an atomic weight that is a whole number. The *fractional* atomic weight of an element is merely the average of the weights of a mixture of isotopes. Some elements consist of as many as ten distinct isotopes.

A FEW EXAMPLES OF ISOTOPES

ELEMENT	ATOMIC NUMBER	ATOMIC WEIGHT	ISOTOPIC WEIGHTS
Lithium	3	6.94	7, 6
Neon	10	20.183	20, 22, 21
Magnesium	12	24.32	24, 25, 26
Chlorine	17	35.457	35, 37
Argon	18	39.94	40, 36
Potassium	19	39.10	39, 41
Zinc	30	65.38	64, 66, 68, 70

366. Illustration of Thomson's method. The method that enabled Thomson to prove that neon is a mixture of atoms of at least two different weights can be illustrated in the following way:

Everyone knows that a magnet attracts iron. Now if we should shoot iron bullets of two different weights from the gun *A* (Fig. 166) to the target *C*, the path lying close to the powerful magnet *B*, the *lighter* bullets in passing the magnet *B* would be pulled more out of their straight-line course than would the *heavier* ones. They would strike the target *C* at a point *D*, whereas the less deflected heavier bullets would strike at *E*. If we could make all the necessary measurements, we could calculate the weights of the two kinds of bullets from the two deflections, *D* and *E*.

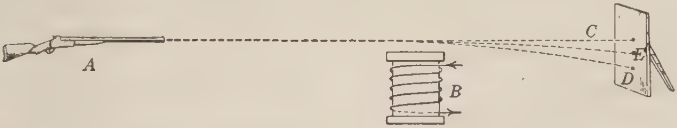


FIG. 166. Illustration of Thomson's method of proving the existence of isotopes

Instead of bullets, Thomson shot charged gas ions of neon past a powerful magnet, and had them strike a photographic plate as a target. After the plate was developed the deflections were measured and the weights of the two varieties of neon atoms were calculated.

CHAPTER SUMMARY IN QUESTION FORM

1. In the study of such things as "elements" and "compounds" what advantage is gained by classifying them into different groups?

2. What is the basis of the natural classification of the elements now used by chemists?

3. (*a*) Explain clearly what is meant by the term *atomic number*. (*b*) What is the relation between the atomic number of an element and the number of satellite electrons in the atom of the element?

4. Explain how the elements are arranged in the periodic table on page 289.

5. (*a*) State the periodic law. (*b*) Who first announced it?

6. Show how each group of elements is divided into "families" of elements.

7. State three ways in which the elements constituting a family resemble each other.

8. State three ways in which the periodic law has been of great service in the development of the science of chemistry.

9. (*a*) How many vacant places remain in the table of the periodic arrangement of the elements? (*b*) What do these vacant places indicate?

10. What name is given to two or more atoms of an element that have different atomic weights?

THOUGHT QUESTIONS

1. Explain why some elements have fractional weights and others do not.

2. (*a*) Predict the approximate atomic weights of the unknown elements. (*b*) Do you think it would be possible also to predict the properties and chemical conduct of these unknown elements?

FOR HONOR STUDENTS

Write a theme on the subject "Atomic Numbers" which will include the following topics: (*a*) meaning of term; (*b*) diagrams of the atoms of a number of elements showing the atomic number of each; (*c*) how the atomic number serves as a natural classification of the elements; (*d*) how this classification has been of great service to the chemist.

CHAPTER XXVI

THE CHLORINE FAMILY

A Family of Four Very Similar Elements

NAME	ATOMIC WEIGHT	MELTING POINT	BOILING POINT	COLOR AND STATE
Fluorine (F) . . .	19.00	– 223°	– 187°	Pale-yellowish gas
Chlorine (Cl) . . .	35.457	– 101.6°	– 34.6°	Greenish-yellow gas
Bromine (Br) . . .	79.916	– 7.2°	58.7°	Red liquid
Iodine (I)	126.932	113.5°	184.3°	Purplish-black solid

367. The family. These four elements form a strongly marked family, and illustrate very clearly the way in which the members of a family in a periodic group resemble each other, as well as the character of the differences which we may expect to find between the individual members. The four elements of the family are often called the *halogens,* a word meaning "producers of salt." Chlorine has already been studied in Chapter XV. The student should review that chapter in connection with the present one.

Fluorine

368. General discussion. It is safe to say that the student of this text has never seen fluorine. Few people have. This is because the element has been difficult to prepare and has no uses. However, its compounds are of considerable importance. Fluorine is a pale-yellowish gas. It is extremely active, decomposing water with violence and combining with hydrogen to form a gas known as hydrogen fluoride (HF). Of course such an active element would not occur free in nature. Its most important natural compounds are the minerals *fluorite* (CaF_2), the source of all fluorine compounds, and *cryolite* (Na_3AlF_6), which made possible the production of aluminum. Traces of fluorides are also to be found in bones and in the enamel of the teeth.

369. Preparation. Because of its great activity fluorine is difficult to liberate from its compounds. The French chemist Moissan in 1886 finally succeeded in obtaining it in a free state. It is now usually prepared by the electrolysis of melted potassium hydrogen fluoride (KHF_2) in copper vessels.

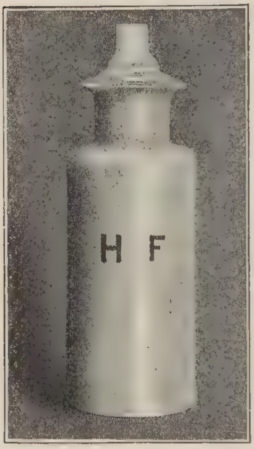


FIG. 167. A wax bottle for holding hydrofluoric acid

370. Hydrogen fluoride (HF); hydrofluoric acid. Hydrogen fluoride is a liquid of low boiling point (19.4°). It is prepared by the action of sulfuric acid on the mineral fluorite (CaF_2), thus:

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2\,HF$$

It is soluble in water in all proportions, forming *hydrofluoric acid*. This is not as strong an acid as is hydrochloric acid, but it has a peculiarly destructive action on skin and flesh and must be handled with great care. It is kept in bottles made of wax (ceresin) (Fig. 167), because it acts on glass.

371. Action on silica and glass. Hydrofluoric acid is the only acid that acts readily on silica (SiO_2) and its compounds, which include sand, quartz, glass, and many minerals; and its practical uses depend upon this fact. In this reaction the element silicon is converted into silicon fluoride (SiF_4), which is a gas:

$$SiO_2 + 4\,HF \longrightarrow \overline{SiF_4} + 2\,H_2O$$

The chief use for hydrofluoric acid is in chemical analysis and in etching (frosting) glass. Practically all electric-light bulbs now made are frosted. They are etched on the *inside* by filling the bulb for a short time with hydrofluoric acid. Etching a design on glass is accomplished by covering the glass with wax, scratching the design through the wax, and then exposing the prepared surface to fumes of gaseous hydrogen fluoride or wetting it with hydrofluoric acid. The wax is then removed by a suitable solvent, leaving the design etched on the glass.

Bromine

372. Properties and occurrence. This element, discovered by the French chemist Balard in 1826, is a heavy dark-red liquid which boils at 58.7° and freezes at $-7.2°$. It vaporizes readily at ordinary temperatures. This vapor has an offensive odor and is very irritating to the eyes and throat. One volume of the liquid dissolves in about 100 volumes of water, and it is readily soluble in carbon tetrachloride and similar solvents. It resembles chlorine in its chemical conduct except that it is less active.

373. Occurrence. All salt waters contain a small percentage of the ion Br^-. When these waters are evaporated the bromine is deposited as a compound of bromine and a metal (generally calcium or magnesium). These compounds are known as *bromides.* The salt waters of Michigan and the Ohio River valley are the richest in bromine and serve as the source of the bromine of commerce.

374. Preparation. The methods used for preparing chlorine in the laboratory (§ 210) serve also for the preparation of bromine (Fig. 168).

$$MnO_2 + 2\,NaBr + 2\,H_2SO_4 \longrightarrow Na_2SO_4 + MnSO_4 + 2\,H_2O + Br_2$$

Commercially it is prepared chiefly by passing an electric current through salt waters containing bromides. Bromine and some chlorine are liberated; the chlorine, however, assists in the reaction, since it decomposes the unchanged bromides, liberating bromine, thus:

$$2\ NaBr + Cl_2 \longrightarrow 2\ NaCl + Br_2$$

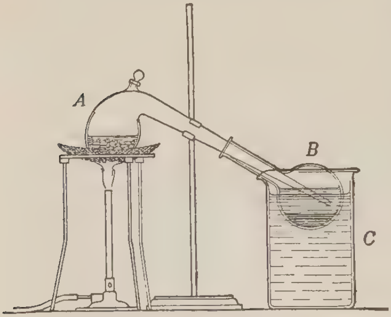


FIG. 168. Laboratory preparation of bromine

In the laboratory the compounds used in the preparation of bromine are placed in the retort *A* and heated. The bromine is set free and is distilled into the receiver *B*, which is kept cold by water in *C*

375. Hydrogen bromide (HBr); hydrobromic acid. Hydrogen bromide is a colorless gas resembling hydrogen chloride except that it is less stable (that is, more easily decomposed). Its solution in water constitutes *hydrobromic acid.* The salts of hydrobromic acid are known as *bromides.* They resemble the chlorides in their properties.

376. Uses. At present the largest use of bromine is in the manufacture of ethylene bromide ($C_2H_4Br_2$), which is a constituent of "ethyl gasoline." It is also used in making certain dyes and medicines and in the preparation of bromides. Silver bromide (AgBr) is used extensively in photography, while sodium bromide and potassium bromide are used as drugs.

Iodine

377. General discussion. Iodine was discovered in the ashes of sea plants by the French chemist Courtois in 1812. It differs from the other halogens in that it is a purplish-black, shining, crystalline solid. When warmed it gives off a beautiful violet vapor. It is only very slightly soluble in water, but readily dissolves in carbon tetrachloride and in alcohol. It resembles chlorine in its chemical conduct, but is even less active than bromine. Even a very small amount of free iodine colors starch blue — a reaction which is used to detect the presence of both iodine and starch.

Like bromine, iodine occurs as an ion (I^-) in ocean water in very small *percentages* but in a very large total quantity. It is absorbed from the water by certain sea plants, and is found in their ashes; it is also found in Chile as a constituent of Chile saltpeter. In very minute quantities it is a constituent of most natural waters, and it is an essential constituent of the thyroid gland of animals. In some instances at least, the disease of this gland known as *goiter* appears to be due to a deficiency of iodine.

378. Preparation. In the laboratory iodine is prepared in the same way as is bromine, using NaI in place of $NaBr$ (§ 374). Commercially iodine was formerly obtained entirely from the ashes of seaweed (*kelp*), and a limited quantity is still obtained from this source. Most of our supply comes from the beds of Chile saltpeter.

379. Hydrogen iodide (HI); hydriodic acid. Hydrogen iodide is a colorless gas, but is less stable than the corresponding compounds of the other halogens. Its solution in water constitutes *hydriodic acid.* The salts of this acid are called *iodides*; these in general resemble the chlorides and bromides.

380. Use. A solution of iodine and potassium iodide in alcohol is known as *tincture of iodine* and constitutes one of our most common antiseptics, as does also iodoform (CHI_3). Silver iodide (AgI) is largely used in photography. Potassium iodide (KI) is used in medicine, and iodine has many uses in chemical analysis.

381. Electrochemical series of halogens. Just as the metals can be arranged in a series in which the higher ones displace the ions of the lower ones in the series (§ 256), so the halogen elements can be arranged in a similar series in the order

Fluorine, chlorine, bromine, iodine

For example, chlorine gas bubbled into a solution containing the ion Br^- or I^- takes away the excess electron from either of these ions and liberates them as free elements:

$$Cl_2 + 2(K^+, Br^-) \longrightarrow 2(K^+, Cl^-) + Br_2$$
$$Cl_2 + 2(K^+, I^-) \longrightarrow 2(K^+, Cl^-) + I_2$$

382. Test for bromide or iodide ions. In giving the test for the chloride ion (§ 315) it was stated that a solution of silver nitrate when added to a solution of a chloride gives a white precipitate that is insoluble in nitric acid. Unfortunately, bromides and iodides also give a precipitate with silver nitrate, and while these precipitates (AgBr and AgI) are not entirely white, they may be so nearly so as to be confusing. If we are uncertain as to whether the solid we are testing is a chloride, a bromide, or an iodide, we can easily distinguish between the three in the following way: Pour a few drops of the solution of the solid into a test tube half full of water, and add about 2 cc. of carbon tetrachloride (Fig. 169). Next add a few drops of chlorine water and shake the mixture vigorously. If the solid you are testing is a chloride, no reaction will take place; but if it is a bromide or an iodide, the element will be liberated and will dissolve in the carbon tetrachloride. This solution soon settles to the bottom of the tube, colored brownish red if bromine is present, and violet if iodine is there.

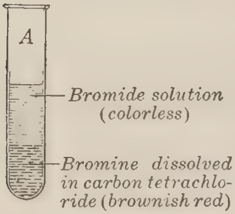

A
Bromide solution (colorless)
Bromine dissolved in carbon tetrachloride (brownish red)

FIG. 169. Testing for bromide ions or iodide ions

A more delicate test for free iodine consists in adding a little starch paste to the solution of iodine. The starch is colored an intense blue by the iodine.

383. Properties of the halogens contrasted. By studying the table at the head of this chapter it will be seen that the halogens exhibit a more or less regular gradation of properties. *This is characteristic of a periodic family.* Fluorine is a light, slightly colored gas, chlorine is a heavier gas with more marked color, while bromine is a red liquid, and iodine a nearly black solid. Their melting points and boiling points *increase with their atomic weights* (see table). Their affinity for hydrogen and the metals, on the other hand, *decreases with their atomic weights,* that of fluorine being the greatest and that of iodine the least. Fluorine and bromine do not combine with oxygen; chlorine forms unstable oxides, and iodine much more stable ones. In an electrochemical series they displace each other from their salts.

CHAPTER SUMMARY IN QUESTION FORM

1. (*a*) Name the halogens. (*b*) Give the color and state of each.

2. Why are these elements called "halogens"?

3. (*a*) What compound of fluorine is very largely used in making electric-light bulbs? (*b*) Write the equation for its preparation.

4. Describe the process of etching glass.

5. Name two compounds which together will expel the three most familiar halogens from their salts.

6. (*a*) Illustrate question 5 by writing the equation for the laboratory preparation of bromine. (*b*) Substitute the symbol of iodine for that of bromine wherever it occurs in this equation; what does the equation now represent?

7. Is it true that mercury is the only element that occurs in the liquid state under ordinary conditions?

8. What is the chief commercial source of bromine?

9. State the relation that bromine bears to (*a*) the automobile industry; (*b*) the movies.

10. Arrange on a sheet of paper the following table, inserting the information requested:

FORMULA	NAME	NAME OF WATER SOLUTION	NAME OF COMPOUND FORMED BY REPLACING H WITH K
HBr			
HCl			
HI			
HF			

11. Where in nature do we find most of (*a*) the iodide ions? (*b*) the non-ionized iodine?

12. By what physical property could you easily identify (*a*) chlorine? (*b*) bromine? (*c*) iodine?

13. Write the names of the three most common halogens in the order in which the free element would displace the others from solutions of their salts.

14. A white or nearly white precipitate, insoluble in nitric acid, formed by adding a solution of silver nitrate to a solution indicates the presence of what ions?

15. Suppose you have a white solid, and know that it is either KCl, KBr, or KI. You could tell which of the three it is by dissolving the solid in water, adding first a few drops of carbon tetrachloride and then a few drops of chlorine water, and shaking the mixture well. What results would follow if the solid were (*a*) KCl? (*b*) KBr? (*c*) KI?

16. (*a*) Starch paste turns blue in the presence of what element? (*b*) So far as this test is concerned, does it make any difference whether the element is in a free state or a combined state?

17. What is the common name for a solution of a mixture of iodine and potassium iodide in alcohol?

THOUGHT QUESTIONS

1. Some manufacturers of table salt advertise that their brand contains iodides. Why should this be considered a point worth advertising?

2. (*a*) What gas have we studied that resembles the vapor of bromine? (*b*) How could you distinguish between the two?

3. Were any of the halogens known when oxygen was discovered?

4. Suppose you had potassium iodide and wished to prepare some tincture of iodine. How would you proceed?

5. In which of the following would a reaction take place?

(*a*) $KI + Cl$
(*b*) $NaBr + I$
(*c*) $NaI + Br$
(*d*) $KBr + Cl$
(*e*) $NaCl + I$
(*f*) $KCl + Br$

6. Give the derivation (see dictionary) of each of the following names, and indicate whether or not the name is appropriate: (*a*) chlorine; (*b*) bromine; (*c*) iodine; (*d*) halogen.

7. What weight of potassium iodide would be required for the preparation of 10 g. of iodine?

8. Suppose your hands were stained with iodine. How could you remove the stain?

FOR HONOR STUDENTS

1. The tincture of iodine that you buy at the drug store contains 70 g. of iodine and 50 g. of potassium iodide dissolved in sufficient alcohol to make 1 liter of the solution. Suppose you had potassium iodide but no iodine with which to make this. What weight of this salt would be required to prepare 1 liter of the tincture?

2. Demonstrate either or both of the following experiments before the class and explain fully what happens:

(*a*) Prepare some starch paste and divide it into two parts. Have at hand (1) a solution of iodine in alcohol, (2) a water solution of potassium iodide, and (3) some chlorine water. Ask the class to predict what will happen when starch paste is added to (1); to (2); to (3). See if their predictions are verified. Now add some chlorine water to (2) and account for the results.

(*b*) Place on a sheet of copper a piece of filter paper saturated with a solution containing potassium iodide and starch paste. Does a blue color appear? Attach by a wire the copper plate to the negative pole of a battery, and draw or write on the filter paper with one end of another wire attached to the positive pole of the battery. Explain the results.

CHAPTER XXVII

THE PHOSPHORUS FAMILY

NAME	SYMBOL	ATOMIC WEIGHT	DENSITY	MELTING POINT
Phosphorus	P	31.02	1.82	44°
Arsenic	As	74.93	5.7	—
Antimony	Sb	121.77	6.68	630.5°
Bismuth	Bi	209.00	9.80	271°

384. The family. The elements constituting this family belong in the group with nitrogen and therefore resemble it in a general way. They exhibit a gradation of properties very much like that of the elements in the halogen family, as is shown in the table.

Phosphorus

385. Properties. When we hear the word *phosphorus,* we are apt to think of matches and bones, for it is well known that phosphorus is the substance used to make matches inflammable and that its compounds constitute the principal mineral constituents of bones. The free element is obtained in two chief forms, known as yellow phosphorus and red phosphorus.

Yellow phosphorus, often called *white phosphorus* (although not white), is a nearly colorless, translucent, waxy solid which melts at 44°. It is sold in the form of sticks (Fig. 170) and is the common form of phosphorus. *Red phosphorus* is a dark-red powder.

The two allotropic forms of phosphorus differ widely in properties. The yellow form is very poisonous, is soluble in carbon disulfide, and ignites so readily that it must be kept under water and handled with the greatest care. It is easily cut into pieces, *but this must always be done under water* to avoid ignition. Red phosphorus, on the other hand, does not ignite easily, is not soluble in carbon disulfide, is not poisonous, and has a high melting point. Yellow phosphorus is formed when any form of the element is distilled and its vapor suddenly chilled, as by passing it into cold water. On standing at ordinary temperatures it slowly changes into the red variety; at higher temperatures or by the use of a catalyst (iodine) the change is much more rapid.

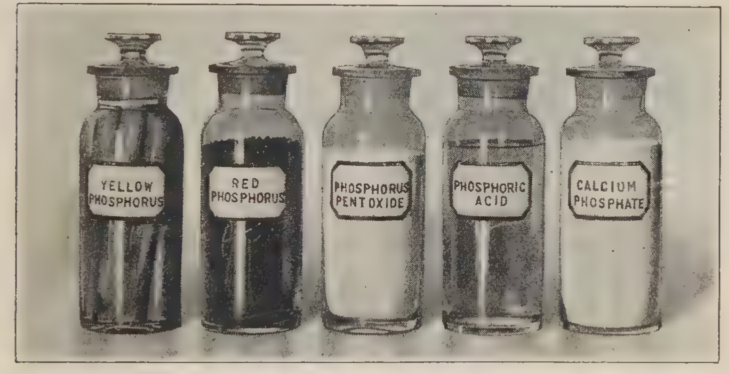


FIG. 170. Phosphorus and some of its most common compounds

386. History and occurrence. Phosphorus has long been known, having been discovered in 1669 by the alchemist Brand while searching for the philosopher's stone. It occurs almost entirely in various mineral forms of calcium phosphate ($Ca_3(PO_4)_2$). *Phosphorite,* the most abundant of these minerals, is almost wholly derived from fossil remains of animals; *apatite* is a crystalline mineral consisting of calcium phosphate together with calcium fluoride or chloride. Calcium phosphate is the chief mineral constituent of the bones of animals, and bone ash is therefore nearly pure calcium phosphate.

387. Preparation. The element is prepared by heating a mixture of calcium phosphate, sand, and carbon in an electric furnace. Phosphorus is liberated as a vapor, and this is condensed under cold water and cast into stick form as the yellow variety. Very little is produced in the United States.

388. Chemical conduct. The most striking property of yellow phosphorus is its affinity for oxygen. Even when exposed to *cool* air it slowly combines with oxygen, and in so doing gives out a pale light, or *phosphorescence* (seen only in a dark place); whence the name *phosphorus,* which means "light-carrier." The heat of the room may raise the temperature of phosphorus to the kindling point, when it burns with a sputtering flame, giving off dense fumes of oxide of phosphorus. It burns with dazzling brilliancy in oxygen and combines directly with many other elements. On account of its great attraction for oxygen it is preserved under water. While phosphorus forms many compounds, only a few of them are of great commercial importance.

389. Oxides of phosphorus. Phosphorus forms two well-known oxides — the trioxide (P_2O_3) and the pentoxide (P_2O_5), sometimes called *phosphoric anhydride.* The pentoxide, a voluminous snow-white powder, is much the better known of the two; it is formed when phosphorus burns in oxygen or air (Figs. 171, 172). *Its most marked property is its great attraction for water.* It has no chemical action upon most gases, so that they can be very thoroughly dried by being passed through properly arranged vessels containing phosphorus pentoxide.

390. Sulfides of phosphorus. When phosphorus and sulfur are brought together under certain conditions, they combine to form *phosphorus sesquisulfide* (P_4S_3). This is a dark-colored solid and is largely used in making matches. There are several other less important sulfides of phosphorus.

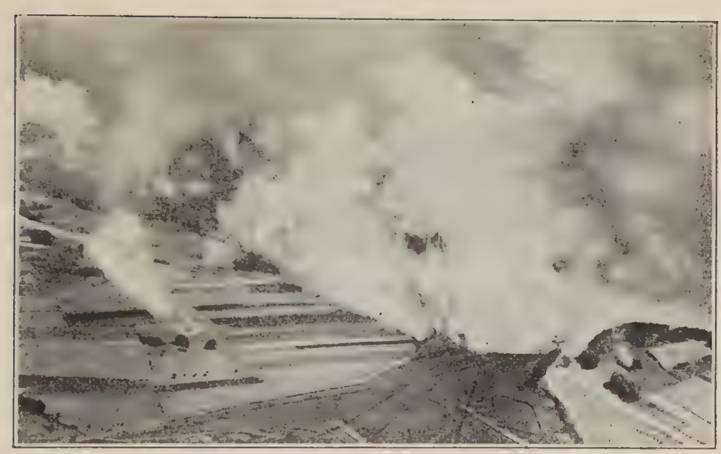


FIG. 171. The use of phosphorus in the World War to conceal troops

When troops were ready for an attack, shells filled with phosphorus were fired in advance of the lines. When these exploded, the phosphorus burned, forming dense clouds of the oxide which entirely concealed the troops

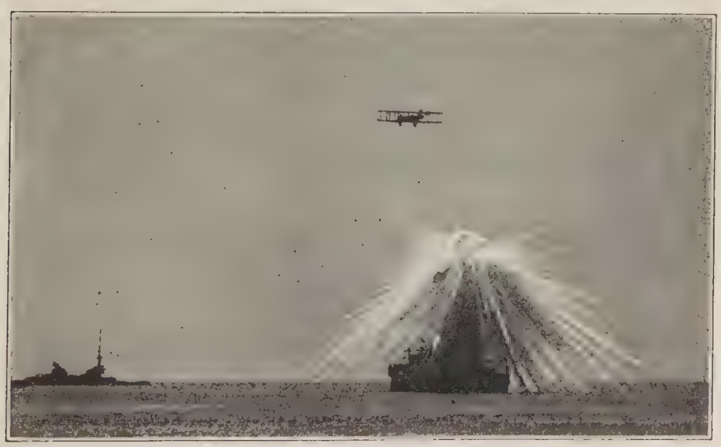


FIG. 172. The use of phosphorus in naval warfare

A phosphorus bomb may be dropped by an airplane upon a ship, enveloping it in a dense cloud, either to conceal its exact location or to make it impossible for it to fire accurately. The figure shows an airplane which has made a "hit" with a phosphorus bomb. (Photograph by United States Army Air Corps)

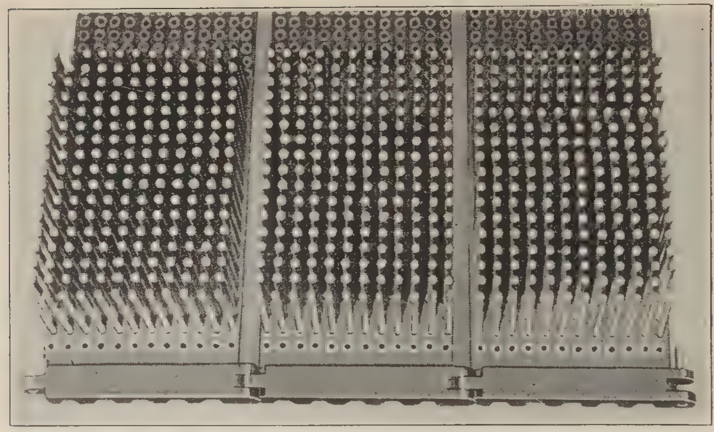


FIG. 173. Match sticks ready for dipping

A plate full of holes into which match sticks are inserted to keep them separated from each other while the free ends are dipped into the liquid preparation to form the match head

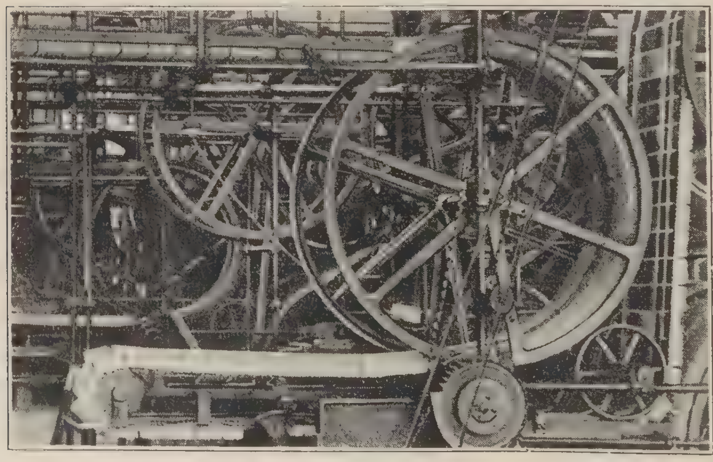


FIG. 174. Forming the match head by dipping the match stick

Plates full of match sticks (the same as shown on Fig. 173, but much reduced in size) are carried on an endless belt in such a way as to dip the free ends of the sticks successively into the liquid preparations that form the bulb and tip, and then to dry the matches

391. Phosphoric acid (H_3PO_4). Phosphorus forms a number of acids, but the only very important one is phosphoric acid (H_3PO_4). The pure compound forms large colorless crystals; ordinarily the acid contains a little water, and it then forms a thick, sirupy liquid (Fig. 170). It is prepared by treating its calcium salt with sulfuric acid:

$$Ca_3(PO_4)_2 + 3\ H_2SO_4 \longrightarrow 3\ \underline{CaSO_4} + 2\ H_3PO_4$$

The calcium sulfate ($CaSO_4$) formed is nearly insoluble and can be separated from the phosphoric acid by filtration.

392. Salts of phosphoric acid; the phosphates. Being *tribasic*, phosphoric acid forms acid salts as well as normal salts. Thus, the following sodium salts are known:

NaH_2PO_4	primary, or monosodium-hydrogen phosphate
Na_2HPO_4	secondary, or disodium-hydrogen phosphate
Na_3PO_4	tertiary, or normal sodium phosphate

The phosphates form an important class of salts. The most important phosphate is calcium phosphate, which is mined in enormous quantities for use as a fertilizer. Ordinary sodium phosphate ($Na_2HPO_4 \cdot 12\ H_2O$) has some uses in medicine. As its formula indicates, it is a hydrated salt, 1 molecule of the salt crystallizing with 12 molecules of water. Most of the normal phosphates are insoluble, and there is no simple test for the phosphate ion.

393. Uses. Yellow phosphorus is used for minor purposes in chemical laboratories. During the World War large amounts were used in generating smoke clouds (P_2O_5) for concealing troops and ships (Figs. 171, 172). The incendiary bullets which proved so disastrous to the Zeppelins during the war contained free phosphorus. *The chief use of phosphorus, however, is in making matches.*

394. Matches. Friction matches containing phosphorus first came into use in 1827, and at present two general varieties are in common use. In the "strike-anywhere" matches, the large head or bulb contains (1) an oxidizing agent, generally potassium chlorate, (2) some material easily oxidized such as sulfur, paraffin, or rosin, (3) a binding substance such as glue, and (4) some filling material like ground glass. The tip of the bulb contains, in addition to the above, a large percentage of phosphorus sesquisulfide (P_4S_3). On friction, the phosphorus is ignited, the combustion being supported by the oxidizing agent and communicated to the wood by the burning paraffin or rosin (Figs. 173, 174).

In the *safety* match red phosphorus, an oxidizing agent, and some gritty material, such as powdered glass, are mixed with glue and placed on the side of the box. The match tip is provided with an oxidizing agent and an easily combustible substance, usually antimony sulfide. The match cannot be ignited easily by friction except on the prepared surface.

Arsenic

395. Occurrence and properties. When we hear the word *arsenic* we are apt to think of a poisonous substance, because it is well known that materials containing arsenic are poisonous. Like phosphorus, the element arsenic is obtained in a number of forms; the usual one is a steel-gray solid. In nature it occurs combined with sulfur as a bright-red or yellow mineral. Small percentages, combined with metals, are present in ores of copper sulfides. In the separation of copper from these ores the arsenic is obtained as a by-product in the form of the oxide As_2O_3. A few years ago it was regarded as a nuisance by the copper-refiners, but it is now in large demand in the manufacture of insecticides.

The element arsenic can be obtained from the oxide by heating with carbon:

$$2\ As_2O_3 + 3\ C \longrightarrow As_4 + 3\ CO_2$$

Arsenic burns when heated in air, forming the oxide As_2O_3.

396. Compounds. When hydrogen is generated in contact with arsenic or its compounds, a *very poisonous*, colorless gas known as *arsine* (AsH_3) is generated. The most familiar compound of arsenic is the oxide As_2O_3, known as arsenic trioxide or *arsenious oxide* or often as *white arsenic*. It is a rather heavy white solid, obtained either as a crystalline powder or in lumps resembling porcelain in appearance. It is very poisonous, from 0.2 to 0.3 g. being a fatal dose. Arsenic also forms a number of acids, the most important of which are *arsenious acid* (H_3AsO_3) and *arsenic acid* (H_3AsO_4). Some of the salts of these acids are of considerable importance.

397. Uses. Arsenic in the free state is little used. About 0.5 per cent of arsenic is added to lead used in making shot, since this makes the lead harder and the shot rounder. The oxide As_2O_3 is used in preparing all the other compounds of arsenic. It is also used in making glass and as a preservative in mounting the skins of birds and animals. Its greatest use is in the preparation of insecticides for spraying trees, vegetables, and cotton crops, and killing parasites on stock.

398. Arsenic insecticides. Several compounds of arsenic have important uses as insecticides. *Paris green* and *Scheele's green* are salts made by treating solutions of copper salts with arsenious oxide. The commercial *lead arsenate* so widely used as a spray (§ 325) is chiefly $Pb_3(AsO_4)_2$, and calcium arsenate is the corresponding calcium salt.

Antimony

399. General. Antimony is a silver-like, brittle, crystalline solid a little lighter than iron. It melts at 630.5° and expands somewhat on solidifying. It is found in nature chiefly in the form of *stibnite* (Sb_2S_3), and the world's supply comes largely from China. It is obtained by heating melted stibnite with iron:

$$Sb_2S_3 + 3\ Fe \longrightarrow 2\ Sb + 3\ FeS$$

It forms a number of compounds which resemble the corresponding compounds of arsenic in composition and properties. Its chief use is in making *alloys* (§ 402), especially the ones known as *type metal* and *Babbitt metal.*

Bismuth

400. General. Bismuth resembles antimony in appearance except that it has a slightly rosy tint. It is a little heavier than iron, but melts at a low temperature (271°). It occurs in nature chiefly in the free state, and our supply comes largely from Bolivia. As with antimony, its chief use is in the making of alloys. The element differs from the other elements of the phosphorus family in that it has practically no acid properties, but acts as a metal in forming salts. Sulfuric and nitric acids dissolve it just as they do copper. When heated in the air it burns, forming the oxide Bi_2O_3. This oxide is soluble in acids, forming salts:

$$Bi_2O_3 + 6\ HCl \longrightarrow 2\ BiCl_3 + 3\ H_2O$$
$$Bi_2O_3 + 6\ HNO_3 \longrightarrow 2\ Bi(NO_3)_3 + 3\ H_2O$$

These salts are hydrated and are colorless, crystalline solids.

401. Action of water on bismuth salts. The salts of bismuth react with water as shown in the following equations:

$$BiCl_3 + H_2O \rightleftharpoons \underline{BiOCl} + 2\ HCl$$
$$Bi(NO_3)_3 + H_2O \rightleftharpoons \underline{BiONO_3} + 2\ HNO_3$$

The compound BiOCl, known as *bismuth oxychloride,* as well as the corresponding *bismuth oxynitrate,* $BiONO_3$, are white solids, the latter having some uses in medicine.

Alloys

402. Nature of alloys. Bismuth and antimony (as well as many other metals), when melted together, thoroughly intermix, and on cooling form a uniform metal-like substance called an *alloy.* Not all metals will mix in this way, and in some cases definite chemical compounds are formed and crystallize out as the mixture solidifies, destroying the uniform quality of the alloy. In general, the melting point of the alloy is below the average of the melting points of its constituents.

Both antimony and bismuth alloy readily with many of the metals. The alloys so formed are heavy, are easily melted, do not oxidize easily nor act upon water, and, in general, are well adapted to many technical uses. The manufacture of alloys constitutes the chief use of these two elements.

FIG. 175. An automatic fire curtain above a door

The fire curtain is held in place by the wires *A*, *A*, which are united at *B* by a link of low-melting alloy. When a fire melts the alloy union, the wires are released and the curtain drops

Antimony gives its alloys the property of expanding slightly in solidifying; this renders them especially useful in typefounding, where lines are to be sharply and precisely reproduced on a cast. *Type metal* consists of antimony, lead, and tin. *Babbitt metal,* largely used for bearings in machinery (for example, the bearing of an automobile crankshaft), consists of antimony and tin, together with a small percentage of copper.

Bismuth is particularly valuable in the production of very low-melting alloys. For example, *Wood's metal,* consisting of bismuth, lead, tin, and cadmium, melts at 60.5°. The low melting point of such alloys is turned to practical account in making safety plugs in boilers, automatic fire curtains (Fig. 175) and automatic water sprinklers in buildings, and many similar devices.

CHAPTER SUMMARY IN QUESTION FORM

1. Name the two chief forms of phosphorus.

2. Which form of phosphorus is (*a*) the more active? (*b*) the more stable?

3. What precautions must we take when working with yellow phosphorus?

4. Give the chemical name and formula of the compound from which phosphorus is obtained commercially.

5. (*a*) What weight of phosphorus is present in your body? (*b*) In what form is it present?

6. Give the most striking property of yellow phosphorus.

7. Name and give the formula of (*a*) a well-known oxide, (*b*) a useful sulfide, and (*c*) an important acid of phosphorus.

8. What name do we apply to an acid like phosphoric acid that has three replaceable hydrogen atoms?

9. Give the names and formulas for the salts which phosphoric acid forms with sodium.

10. What compound of phosphorus is mined in large quantities for use as a fertilizer?

11. What is the chief use of phosphorus?

12. What materials are present (*a*) in the bulb of the match head? (*b*) in the tip?

13. Name three compounds of arsenic of commercial importance.

14. Mention the chief use of arsenic compounds.

15. Many metals when melted together thoroughly intermix. What name is given to the resulting metal-like substance?

16. Supply the missing word: The chief use of antimony and bismuth is for making ______.

17. Supply the missing words: Bismuth, tin, lead, and cadmium make an alloy that is very useful because of its low ______ ______. Its chief use is in making ______.

THOUGHT QUESTIONS

1. (*a*) Write the formulas for the three sodium salts of phosphoric acid. (*b*) Indicate which is normal and which are acid salts.

2. In what connection has phosphorus been referred to in an earlier chapter?

3. Why does cutting a piece of phosphorus in air cause it to ignite?

4. Give the function of each of the materials used in making matches.

5. Give reasons for keeping (*a*) sodium in kerosene, (*b*) phosphorus in water, (*c*) ammonia in rubber-stoppered bottles, and (*d*) hydrofluoric acid in wax bottles.

6. How does an automatic water sprinkler in a building operate to extinguish fires?

7. (*a*) What weight of phosphorus can be obtained from 50 kg. of pure calcium phosphate? (*b*) What weight of pure phosphoric acid?

FOR HONOR STUDENTS

1. Obtain some Wood's metal and mold it into the form of a stirring rod. Stir some boiling water with the rod. Explain the result.

2. Read Chapter XIII (entitled "Matches") in Volume II of "Chemistry in Industry." Write a theme on the subject or report verbally the interesting facts to the class.

CHAPTER XXVIII

SOILS AND FERTILIZERS

403. Formation of soils. Soil results from disintegration of rock. Many agencies contribute to this change, prominent among them being the action of water and air. The glaciers which once covered a large portion of the globe exerted a very powerful grinding effect, breaking off large bowlders and reducing them to a powder.

Water acts in a number of ways. It finds its way into the cracks and crevices, and on freezing expands and so tends to break the rocks; it dissolves out certain rock constituents so that the remainder of the rock tends to crumble; and running water carrying particles in suspension grinds the rocks with which it comes in contact.

Air also acts upon some rocks chemically, while strong winds carrying sand dust exert a powerful sand-blast effect. When plants get a foothold they assist greatly, not only by the mechanical action of their roots but also through the chemical action of the various products formed in their decay. The soil is the result of all these agencies acting through long periods of time (Fig. 10).

404. Different kinds of soil. Since the rocks vary widely in composition, it follows that the resulting soils will vary in a corresponding way. Thus we have limestone soil, formed chiefly by the weathering of limestone; and sandy and clay soils, which are richer in silicates. When plants decay certain acid products are formed, so that soils tend to become acid. Most crops do not thrive on such soil. If the soil contains limestone, the acids will be neutralized as fast as formed and the soil thus kept *sweet*; if the soil does not contain limestone, then ground limestone, or calcium hydroxide, should be added to the soil (Fig. 176).

Soils differ not only in composition but also in their physical properties. Thus, some soils are light and easily allow water and air to circulate through them (these conditions are essential to a fertile soil), while others are compact and impervious to water. Crops do not thrive on wet soils; and such soils must be freed from excess water by drainage.

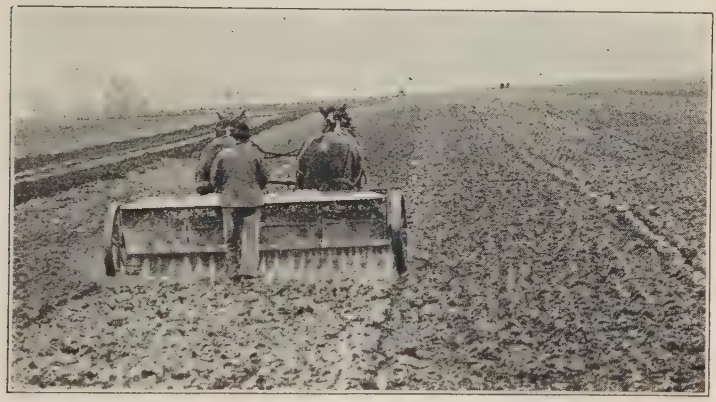


FIG. 176. Neutralizing acidity in soil by an application of calcium hydroxide, or ground limestone

405. Plant food and fertilizers. With the exception of carbon dioxide (and possibly a little oxygen) absorbed from the air, the growing plant derives its nourishment from the soil. It is essential, therefore, that the soil should contain an adequate supply of appropriate plant food, and this includes both mineral matter and organic matter (*humus*).

Moreover, since this supply is continually being drawn upon by the growing plant, it is necessary that the constituents so withdrawn shall be returned to the soil, in order that it may retain its fertility. It is for this purpose that fertilizers are used (Fig. 177).

406. Constituents of fertilizers. While a number of elements are essential to the growth of the plant, experience has shown that in general the fertility of a soil that has the necessary physical properties may be maintained by adding three substances: (1) nitrogenous matter, (2) phosphates of calcium, and (3) compounds of potassium. It seems probable that the elements sulfur, manganese, iron, and possibly boron also play important parts in the growth of plants.

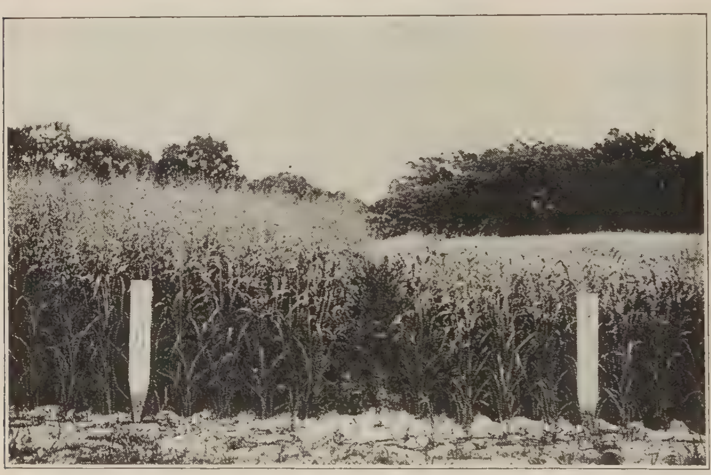


FIG. 177. Effect of fertilizers on the growth of a field of oats

407. Sources of fertilizers. The commercial sources of each of the constituents of fertilizers are as follows:

1. ***Nitrogenous matter.*** This is obtained from a number of sources: sodium nitrate, ammonium sulfate, and cyanamide (§ 577); also nitrogenous organic matter, such as dried blood, the waste from slaughterhouses, fish scrap, and, especially, animal excrements.

2. ***Phosphates.*** Ground bones are especially valuable, since they contain some nitrogen in addition to calcium

phosphate. This source, however, is entirely inadequate, and the great supply comes from the rock phosphates, which contain about 70 per cent of calcium phosphate. These rock phosphates are quarried in large quantities, especially in Florida (Fig. 178) and Tennessee. Since calcium phosphate is nearly insoluble, the rock is ground and then treated with sulfuric acid. This converts the insoluble calcium phosphate into the soluble calcium acid phosphate ($CaH_4(PO_4)_2$):

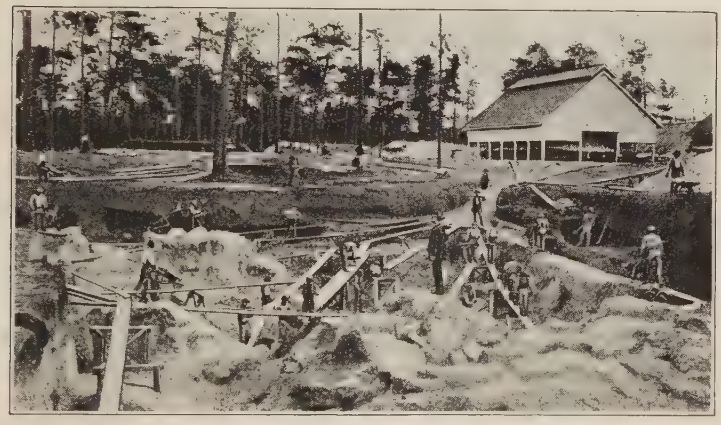


FIG. 178. Mining phosphate rock in Florida

$$Ca_3(PO_4)_2 + 2\ H_2SO_4 \longrightarrow 2\ CaSO_4 + CaH_4(PO_4)_2$$

The calcium sulfate also adds to the value of the fertilizer, furnishing sulfur and improving the physical qualities of the soil. Certain products (slags) formed in the manufacture of steel contain phosphorus and are also used in fertilizers.

3. ***Potassium compounds.*** These are obtained principally from the natural deposits in Germany and France. The United States furnishes a limited supply.

408. Commercial fertilizers. As a rule the fertilizers on the market are mixtures of these three fundamental materials. The composition is varied according to the crop to be grown as well as to the nature of the soil; for example, potatoes demand a fertilizer rich in potassium, while a cereal, such as wheat, is benefited more by one rich in phosphates. Instead of using a fertilizer containing all three constituents, it is preferable to find out by experiment just what plant food is lacking in individual soils and then to make a proper mixture of such fertilizing materials as will furnish the desired food.

409. Utilization of atmospheric nitrogen. With few exceptions plants have not the power of utilizing free nitrogen (§ 265). Moreover, it is inevitable that the supplies of sodium nitrate and ammonium sulfate, which are now the chief nitrogenous products used in the manufacture of commercial fertilizers, will sooner or later become exhausted. More and more we shall have to depend upon the conversion of atmospheric nitrogen into compounds suitable for plant food (§ 407).

CHAPTER SUMMARY IN QUESTION FORM

1. What relation does soil bear to rock?

2. Name four agencies that help to make soil.

3. Give examples of two kinds of soil.

4. What word means "organic plant food"?

5. Name three substances which will maintain the fertility of soils that have the necessary physical properties.

6. Name three chemical compounds which may be added to soil to maintain a supply of nitrogen for growing plants.

(Ammonia, Ammonium sulf [illegible])

7. Name three sources of phosphates.

8. Should you say calcium phosphate is soluble, very soluble, nearly insoluble, or insoluble?

9. Name two compounds, which have value as a fertilizer, that result from the action of sulfuric acid on calcium phosphate.

10. Which of the compounds mentioned in the preceding question is more valuable to the farmer?

11. Name three elements that are made available to plants by adding to the soil a complete fertilizer.

12. What promises to be the future source of the nitrogen necessary for the growth of plants?

THOUGHT QUESTIONS

1. Why do farmers add lime to clay soils?

2. (*a*) Why do wood ashes make a good fertilizer? (*b*) Why are not more of them used?

3. Explain why "it is inevitable that the supplies of sodium nitrate and ammonium sulfate, which are now the chief nitrogenous products used in the manufacture of commercial fertilizers, will sooner or later become exhausted."

4. Give two different methods for changing the nitrogen of the air into fertilizers.

5. What kind of crops enrich the soil?

6. Ground bones are sometimes used as fertilizers, but their action is slow. Explain.

7. How could you find out what mineral products are withdrawn from the soil by different kinds of crops?

FOR HONOR STUDENTS

1. Give examples of soil formation that have come under your observation.

2. In making fertilizers the sulfuric acid used contains about 50 per cent of hydrogen sulfate. What weight of such an acid is necessary for the treatment of 5 tons of rock phosphate containing 70 per cent of calcium phosphate?

3. Read Chapter V (entitled "Maintaining Soil Fertility") in "Chemistry in Agriculture," or Chapter III (entitled "Feeding the Soil") in "Creative Chemistry." Write a theme on the subject or report verbally the interesting facts to the class.

CHAPTER XXIX

SILICON AND BORON

One Very Important Element and Another that has Few Uses

Silicon

410. ***Introduction.*** We are quite ready to grant the importance of oxygen because of its abundance and the fact that it is a constituent of nearly everything in nature. We see at once the supreme importance of carbon because the structures of all living things depend on it; and as the chief constituent of coal and oil it provides us with most of our sources of heat, light, and power. What element should come third in importance? This is not a very profitable question; but it can be said at once that silicon plays the same important part in the solid structure of the world that carbon does in living things. The compounds of silicon make up about 87 per cent of the earth's crust, while the element itself is present to the extent of about 25 per cent. It ranks second only to oxygen in abundance.

411. Preparation and properties. Although so abundant, it is not so familiar as are many other elements of rarer occurrence. This is because it never occurs native, and in pure state has few uses. It can be prepared by heating a mixture of sand (SiO_2) and carbon in an electric furnace:

$$2\,C + SiO_2 \longrightarrow Si + 2\,CO$$

It is a bright, metallic, brittle solid and as an alloy with iron it is used largely for making certain varieties of iron and steel of which we shall learn later.

Silicon occurs in nature chiefly in the form of silicon dioxide (*silica*) (SiO_2) or in the form of salts of silicic acids (*silicates*). These compounds make up almost all the common rocks and soils except limestone. Plants absorb small amounts of silica from the soil, and it is also found in minute quantities in animals, especially in hair, claws, and horns.

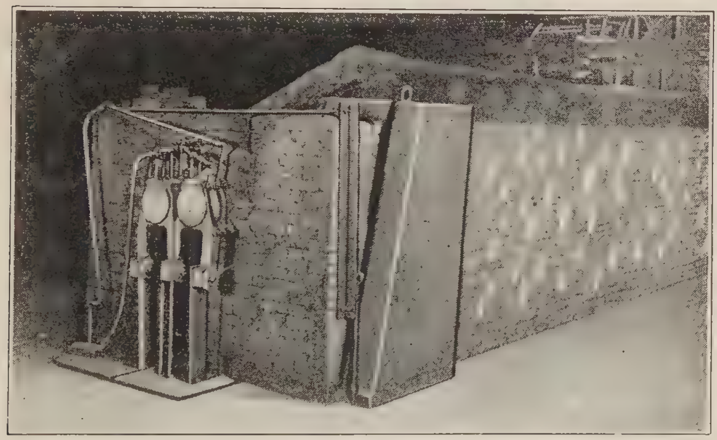


FIG. 179. A carborundum furnace in operation

Coke, sand, common salt, and sawdust are heated in a large resistance furnace, similar to the one used in the manufacture of graphite (Fig. 63). The salt acts as a catalyst, while the destructive distillation of the sawdust keeps the mass porous. This facilitates the escape of carbon monoxide, which then burns on the surface of the furnace as shown in the figure

412. Silicides. As the name indicates, *silicides* are compounds consisting of silicon and some one other element. They are very stable at high temperatures, and are usually made by heating the appropriate substances in an electric furnace.

The most important silicide is carbon silicide (or silicon carbide), best known under the registered trade name *carborundum.* It has the formula CSi. When carbon is heated with sand in an electric furnace, silicon is first liberated (§ 411). Under proper conditions the silicon then combines with excess of carbon to form CSi, and it is in this way that carborundum is prepared.

$$SiO_2 + 3\ C \longrightarrow CSi + 2\ CO$$

Large quantities of this product are made at Niagara Falls (Fig. 179). It can be obtained as perfectly colorless crystals, but as made commercially the crystals have a beautiful purplish-black color due to the presence of small amounts of other elements, chiefly iron. Carborundum is very hard, being surpassed in this property only by the diamond and one or two rare compounds. It is this property which makes it so valuable. It is used as an *abrasive*, that is, as a material for grinding and polishing very hard substances (Fig. 180).

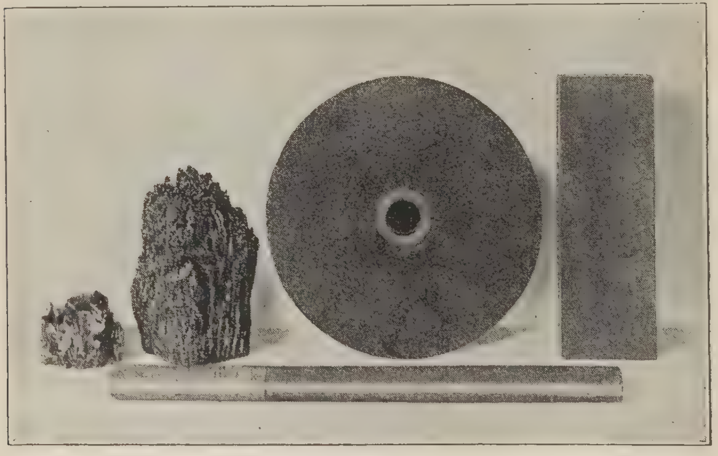


FIG. 180. Crystals of carborundum, and abrasive utensils made of carborundum

413. Silicon dioxide (silica) (SiO_2). This substance is found in a great variety of forms in nature, both in the amorphous and in the crystalline condition. In the form of *quartz* (Fig. 181) it is found in beautiful six-sided prisms, sometimes of great size. When pure it is perfectly transparent and colorless. Some colored varieties are given special names, as *amethyst* (violet), *rose quartz* (pale pink), *smoky quartz* (brown), *milky quartz* (opaque). Other varieties of silicon dioxide, some of which also contain water, are *chalcedony, onyx, jasper, opal, agate,* and *flint. Sand* and *sandstone* are largely silicon dioxide.

The skeletons of certain microörganisms (infusoria) are composed of nearly pure silica. In some localities the skeletons have accumulated in immense deposits, forming a very fine and sharp sand called *infusorial earth.* This material is often used as a scouring-powder, especially in scouring-soaps.

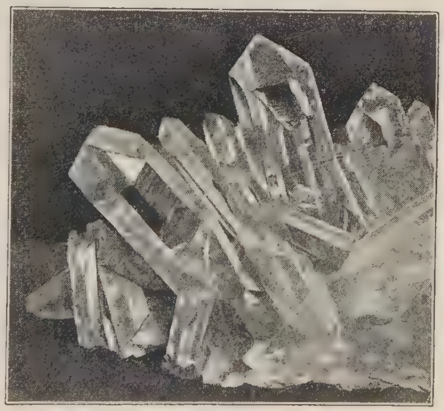


FIG. 181. A cluster of quartz crystals

414. Properties. As obtained by chemical processes, silicon dioxide is an amorphous white powder. In the crystallized state it is very hard and has a density of 2.65. Pure silica begins to soften at about 1600°, and somewhat above this temperature it can be drawn out into threads and blown like glass into tubes and small vessels (Fig. 182). Larger vessels are molded or "built up." These articles are attacked by comparatively few ordinary reagents and do not expand or contract to any appreciable extent with even very great changes in temperature. On this account quartz vessels can be heated red hot and plunged into cold water without cracking. Unfortunately they are quite expensive, but their use is steadily increasing.

Silicon dioxide is very inactive, but is readily attacked by hydrofluoric acid (§ 371). When it is heated to high temperatures with compounds of the metals, especially the carbonates and sulfates, *silicates* (salts of silicic acids) are formed as follows:

$$Na_2CO_3 + SiO_2 \longrightarrow Na_2SiO_3 + CO_2$$
$$Na_2SO_4 + SiO_2 \longrightarrow Na_2SiO_3 + SO_3$$

This is the most important reaction in making glass (§ 425).

FIG. 182. Vessels of pure quartz

415. Silicic acids. Silicon forms two simple acids, *orthosilicic acid* (H_4SiO_4) and *metasilicic acid* (H_2SiO_3). Orthosilicic acid is formed as a jelly-like substance when orthosilicates are treated with strong acids. If one attempts to dry this jelly it loses water, passing into metasilicic acid (common silicic acid):

$$H_4SiO_4 \longrightarrow H_2SiO_3 + H_2O$$

When dried still further, metasilicic acid breaks up into silica and water, thus:

$$H_2SiO_3 \longrightarrow H_2O + SiO_2$$

416. Salts of silicic acids; silicates. A number of salts of the orthosilicic and metasilicic acids are found as minerals in nature. Thus, *mica* ($KAlSiO_4$) is a salt of orthosilicic acid.

417. Condensed silicic acids. Silicon can form a great many *complex* acids. They are formed from two or more molecules of orthosilicic acid, which combine together with the loss of water. These are called *condensed silicic acids.* For example,

$$3\ H_4SiO_4 \longrightarrow H_4Si_3O_8 + 4\ H_2O$$

Salts of these acids make up the great bulk of the earth's crust. For example, *feldspar* has the formula $KAlSi_3O_8$ and is a salt of the acid $H_4Si_3O_8$, whose formation is shown in the last equation. It is by far the most abundant mineral in the world. *Kaolin* has the formula $H_4Al_2Si_2O_9$ or, as commonly written, $Al_2Si_2O_7 \cdot 2\ H_2O$. *Granite* is made up of crystals of feldspar and mica cemented together with silica.

418. Water glass. Sodium silicate and potassium silicate differ from the silicates of the other metals in that they are soluble in water. *Water glass* is a solution of a mixture of sodium silicates. It is a thick, sticky liquid made by melting sand with sodium carbonate. It is used to give a glazed, waterproof surface to porous materials, such as wood, stone, and plaster; to make curtains noninflammable; as a glue for mending glass and pottery and for gluing strawboard boxes; and in making cheap soaps.

Boron

419. General discussion. Boron is a gray solid, difficult to prepare, and in the free state but little used. It is found in nature in many minerals and in many places, but at present the world's supply of boron compounds comes from the Mojave Desert in California. The two sources of production are the mineral *rasorite* ($Na_2B_4O_7 \cdot 4\ H_2O$) and the salts of Searles Lake (Fig. 253). The most important compounds of boron are boric acid, boric oxide, and borax.

420. Boric acid (H_3BO_3). This is a white solid, slippery to the touch, and having exceedingly feeble acid properties. It is a mild antiseptic and is used in medicine.

421. Boric oxide (B_2O_3). When boric acid is heated it loses water and forms the anhydride B_2O_3,

$$2\,H_3BO_3 \longrightarrow B_2O_3 + 3\,H_2O$$

This is a clear, glassy solid that resembles silica in appearance and chemical conduct.

422. Sodium tetraborate ($Na_2B_4O_7$). If we add sodium hydroxide to boric acid we do not get the sodium salt we should expect, namely, Na_3BO_3, but one that has the formula $Na_2B_4O_7$ and is called *sodium tetraborate.* When this is crystallized from water at ordinary temperatures a hydrate is deposited having the formula $Na_2B_4O_7 \cdot 10\,H_2O$. This compound is called *borax.*

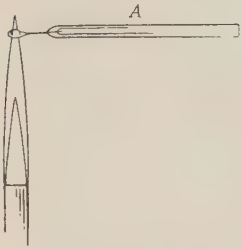


FIG. 183. Borax-bead test

One end of a platinum wire is sealed in the glass handle *A*, the other end being made into a loop. The loop is dipped into powdered borax and then into the material to be tested. The borax is melted in a Bunsen flame and the color of the bead observed

423. Borax ($Na_2B_4O_7 \cdot 10\,H_2O$). Borax is the most important compound of boron, and about four hundred tons are produced daily in California. It is a white solid and crystallizes in large crystals. When borax is heated it swells up in a sort of froth, owing to the escape of steam, and this soon melts to a clear glass. The glass has the property of easily dissolving many metallic oxides, and this fact is turned to account in working with metals. When two pieces of metal are to be joined by the use of some kind of solder, the surfaces must be clean and free from oxide. Brass is joined by melting borax over the joint to clean the metal and then using a low-melting brass as a solder (brazing). Metallic oxides dissolved in melted borax often color the borax glass with characteristic tints. On this account little beads of borax are used in testing for the presence of such metals (Fig. 183).

Borax is extensively used as a constituent of glass, and of enamels and glazes for both metal ware and pottery. It is often used in our homes to soften hard water, and as a mild alkali instead of soap.

CHAPTER SUMMARY IN QUESTION FORM

1. To what element is silicon second in abundance?

2. Sand and sandstone are composed largely of what compound?

3. What general term is applied to compounds containing silicon and some other element?

4. Fill in the missing words: Carbon silicide is known under the trade name of ------. It has the formula ------, and is used as an ------. It is manufactured at ------ ------ because ------ ------ ------.

5. Name three varieties of silicon dioxide found in nature.

6. A beaker composed of quartz is similar in many respects to one composed of glass but differs in one important property. What is this property?

7. Silica, though insoluble in most reagents, dissolves in a certain acid. (*a*) Name the acid and (*b*) state what practical use is made of this reaction.

8. (*a*) What two compounds are formed when a mixture of silicon dioxide and sodium carbonate is heated to a high temperature? (*b*) What practical use is made of this general reaction?

9. (*a*) Give the name of the most abundant of all minerals. (*b*) What elements does it contain?

10. (*a*) What name is applied to a solution of sodium silicates? (*b*) Name two uses of this solution.

11. What locality is the source of the greater part of the world's supply of boron?

12. Give the name and composition of the mineral which is the chief source of all boron compounds.

13. (*a*) Give the name and formula of the most important compound of boron, and (*b*) state four uses of this compound.

14. Many salts, such as sodium tetraborate ($Na_2B_4O_7$), when crystallized from water are found to have formed compounds with the water. (*a*) What is the general name for such compounds (§ 86)? (*b*) What is the name given to the water held in combination? When such compounds are heated the water is expelled. (*c*) What word is applied to the resulting compound?

15. Illustrate the facts stated in question 14 by reference to borax.

16. Why is borax used in the laboratory for making bead tests?

THOUGHT QUESTIONS

1. Give an example in which an electric current causes a chemical reaction (*a*) by the heat the current produces; (*b*) by electrolysis.

2. How could you distinguish between a quartz crystal and a diamond?

3. Could you tell by the physical properties of a compound whether it contained water of hydration?

4. Calculate the molecular weight of each of the compounds represented by the following formulas: (*a*) $BaCl_2 \cdot 2\,H_2O$; (*b*) $Na_2B_4O_7 \cdot 10\,H_2O$. (*c*) Name each of the compounds.

5. When you buy one ton of borax, what weight of water of hydration are you buying?

FOR HONOR STUDENTS

1. Carbon and silicon are in the same group in the periodic arrangement of the elements (p. 289). Study the formulas and reactions of their compounds and see if you can find any points of resemblance.

2. Read what Slosson has to say about carborundum in "Creative Chemistry"; also read Chapter II (entitled "Abrasives") in Volume I of "Chemistry in Industry," and report items of interest to the class.

CHAPTER XXX

SILICATE INDUSTRIES

Glass, Clay Products, Enamels, Cement

424. *Introduction.* Sand, clay, limestone, and feldspar are the raw materials in a number of most important industries. Among these are the manufacture of *glass, enamels, cement,* and *clay products* such as brick, tile, pottery, and chinaware. These are sometimes called the silicate industries because in each case the finished product is a mixture of silicates. These are salts of the various silicic acids, in which the metals are chiefly sodium, potassium, calcium, and aluminum.

425. Glass. Glass is a mixture of certain silicates that has been *completely melted* and then cooled without crystallization. It is really an undercooled liquid (§ 76), although it is as rigid as a true solid. The silicate mixture is prepared by melting together at a very high temperature materials that contain the necessary metals (such as sodium and calcium) together with an excess of sand (SiO_2). The following equations illustrate the reactions that take place:

$$Na_2CO_3 + SiO_2 \longrightarrow Na_2SiO_3 + CO_2$$
$$Na_2SO_4 + SiO_2 \longrightarrow Na_2SiO_3 + SO_3$$
$$CaO + SiO_2 \longrightarrow CaSiO_3$$

The excess of silica then combines with these simple silicates to make more complex ones.

426. Molding and blowing glass. As melted glass cools it becomes very thick or *plastic,* and while in this condition can be worked into a great variety of shapes that keep their form when cold. The way in which the melted mixture is handled in the glass factory depends upon the character of the object to be made.

Many articles, such as bottles, are made by blowing the plastic glass into hollow molds of the desired shape. The mold is opened, a lump of plastic glass (on the end of a long hollow tube) is lowered into it, and the mold is then closed. By blowing into the tube the glass is forced into the shape of the mold just as an inner tube is blown out against the sides of an automobile casing. The mold is then opened (Fig. 184) and the object lifted out. The top of the object must be cut off at the proper place and the sharp edges rounded off in a flame. Bottles are now more often made by machinery, in which the bottle is blown in the mold by compressed air. Other objects, such as lamp chimneys, glasses, and beakers, are revolved while being blown in the mold, and have no ridge showing where the mold closes.

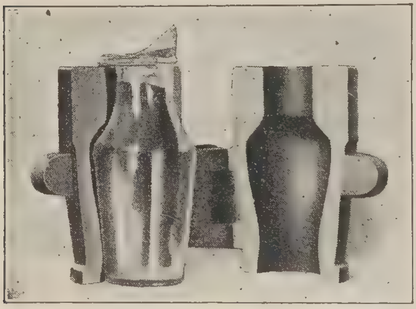


FIG. 184. A glass bottle in its mold

The mold has been opened and the bottle is ready to be removed and finished by rounding its mouth

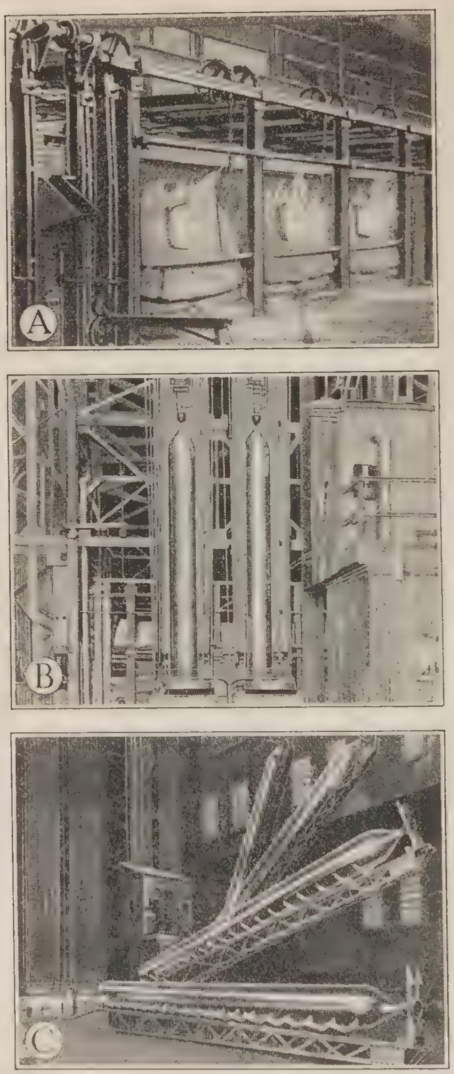
427. Window glass. Window glass has long been made from cylinders of glass blown by skilled glass-blowers, but mouth-blowing has been replaced almost entirely by mechanical methods, as shown in Fig. 185. Increasing amounts are also being made by passing the plastic glass between hot rollers, just as laundry articles are passed between the rolls of a clothes-wringer. Plate glass is cast into flat slabs, which are then ground and polished to perfectly plane surfaces.

428. Varieties of glass. By the proper selection of materials a great variety of glass can be made. Window glass and bottle glass are chiefly a mixture of silicates of sodium and calcium. While we think of glass of this kind as insoluble, nevertheless it will not serve for beakers in which strong chemicals are heated. For such uses some boric acid is added along with the sand, so that the resulting product is a *borosilicate* of the metals present. A sodium-aluminum borosilicate containing a large percentage of free silica, known by the trade name *pyrex glass*, is able to stand sudden changes of temperature and is not easily broken. Optical glass, imported from Germany before the war, but now made in the United States, owes its brilliancy to the presence of lead silicate. Cheap imitations of gems are made from glass rich in lead.

429. Color of glass. Small amounts of certain metals give characteristic colors to glass. For example, cobalt compounds give a blue color, those of manganese a pale purple (amethyst) tint. Gold produces the finest ruby-red color; cuprous oxide as well as the element selenium gives glass a similar color. The tail-lights of automobiles are mostly selenium glass. The sand used in glass-making must be very pure; otherwise iron, which is the most common impurity, will color the glass green, as is usual in cheap bottles.

In most cases the color is due to a colored silicate formed from the metal used. In other cases, as with gold and selenium, the color is due to the metal itself, scattered through the glass in exceedingly small particles.

430. Aluminum silicates. When feldspar ($KAlSi_3O_8$) is decomposed by weather agencies (Fig. 10), soluble potassium compounds are formed which find their way into the soil. At the same time insoluble aluminum silicate is formed which is carried along by running water and is sometimes deposited in the bed of streams in nearly pure condition known as *kaolin* ($Al_2Si_2O_7 \cdot 2\,H_2O$). More often it becomes



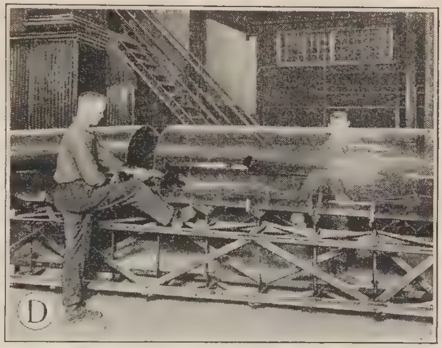
The materials used in making window glass — chiefly lime, sand, and sodium carbonate (or a mixture of sodium sulfate and charcoal) — are heated in furnaces until the reactions are complete and a molten glass is formed

The molten glass is next formed into cylinders as follows: The flattened end of a hollow rod is dipped into the molten glass and the rod slowly raised. Air is forced through the rod, so that the thick liquid glass clinging to the end of the rod is formed into a cylindrical shape as the rod is raised, retaining this shape as the glass hardens

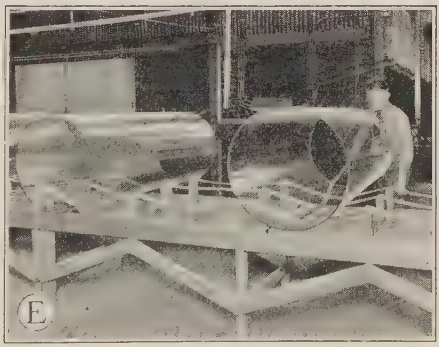
The large cylinders, sometimes 40 ft. in length and 2 ft. to 3 ft. in diameter, are next lowered to a horizontal position by means of suitable machinery

FIG. 185, A, B, and C. The manufacture of window glass

The large cylinders of glass are next cut into shorter cylinders so that they can be handled conveniently



The shorter cylinders are next cracked lengthwise by drawing the hot end of a rod along the glass and suddenly chilling the hot part of the glass



The cracked cylinders are then placed on a flat surface in a large furnace. As the glass gets hot, it softens and slowly opens in the form of a large flat plate. The plate is then removed from the furnace, and after cooling is cut into panes of the desired size

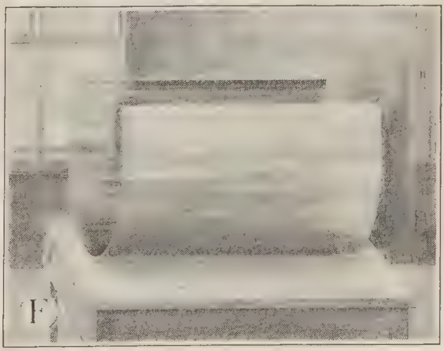


FIG. 185, D, E, and F. The manufacture of window glass

Photographs by courtesy of the Pittsburgh Plate Glass Company mixed with sand and other materials and is then called *clay*. *Kaolin, as well as clay, when mixed with water under proper conditions forms a plastic mass* which can be molded or fashioned into any desired shape. Objects of this kind, when baked in an oven, or *kiln*, keep their shape but become hard and brittle. The making of brick, tile, pottery, and chinaware is based on these properties.

431. Clay products. The crudest forms of clay products, such as porous brick and drain tile, have little chemistry involved in their manufacture. A suitable clay is molded into the required form, dried, and then burned in a kiln, but not to a temperature at which the materials soften. In this process the nearly colorless iron compounds in the clay are converted into colored compounds which give the usual red color to these articles. In making *vitrified brick* the temperature is raised to the point at which melting just begins, so that the brick is partially changed (at least on the surface) to a kind of glass.

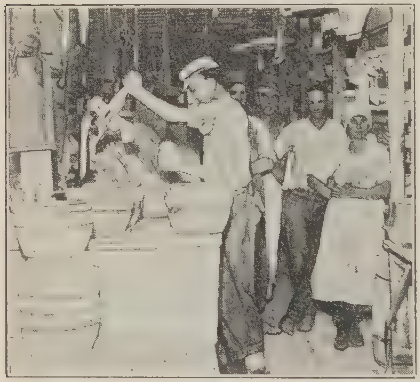


FIG. 186. Molding pottery

Pressing plastic clay into molds by a hand press

432. White pottery. This name is applied to a variety of articles, from the crudest porcelain to the finest chinaware. Although the details of the manufacture of the articles differ, the fundamental processes are the same and may be described under three heads, namely, (1) the body of the ware, (2) the glaze, and (3) the decoration.

1. ***The body of the ware.*** The materials used consist of an artificial clay made by mixing kaolin, plastic clay, and

powdered feldspar. This mixture is plastic and is worked into the desired shape by molds (Fig. 186) or on a potter's wheel. The ware is then dried and burned in a kiln (Fig. 187) until vitrified, and in this form is known as *bisque*. This is usually porous and must therefore be glazed so that it will not soak up water.

2. ***The glaze.*** The glaze is a fusible glass which is melted over the surface of the body. The glaze is made of quartz, feldspar, and various metallic oxides, often mixed with a little boric oxide. These materials are finely ground and are mixed with water to form a paste. Sometimes the materials are first melted together to a glass, which is then powdered and made into the paste. The bisque is dipped into the glaze paste, dried, and fired until the glaze materials melt and flow evenly over the surface.

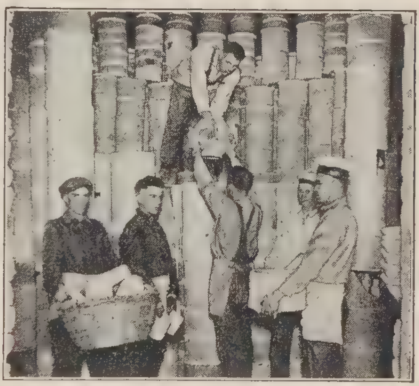


FIG. 187. Inside a kiln

Stacking pottery in the kiln preparatory to firing it

3. ***The decoration.*** If the article is to be decorated, the design may be painted upon the body before glazing, or it may be painted upon the glaze and the article fired again, the color pigments melting into the glaze. In the former case the pigments used are, as a rule, metallic oxides of various colors; in the latter case they are often colored glasses.

433. Enamels. Enamels are glazes melted onto surfaces of various kinds, chiefly metal surfaces, to make the object look like porcelain, and to protect the surface from rust or chemical action. Granite-ware cooking vessels, bath-tubs, and automobile number plates are familiar examples. The finished enamel must expand and contract with changes in temperature at the same rate as the metal under it or it will crack or chip off. Of course it must be able to stick tightly to the metal.

434. Cement. The name *cement* is ordinarily applied to those mortars that have the property of *hardening in water as well as in air*. These cements are silicate bodies, but have in them much more of the basic oxides and less silica than does glass. When ground fine and mixed with water they undergo complex reactions resulting in the formation of a hard, rocklike mass. A number of different classes of cements are known, the most important of which is called *Portland* cement.

435. Manufacture of Portland cement. The materials most commonly employed are limestone and clay or shale, although anything that is similar in composition to these materials may be used.

The materials are coarsely ground separately and are then mixed together in the proper proportions and finely powdered. The resulting mixture is put in a furnace and burned to a temperature just short of fusion, at which temperature it vitrifies, forming a grayish mass known as *clinker*. Finally, the clinker is ground to a fine powder. The mineral gypsum is often added in the process; this acts as a negative catalyst, slowing up the hardening, or *setting*, of the cement.

436. Importance of cement. The importance of cement in the construction industries increases each year. It is often used in place of mortar in the construction of brick buildings. Mixed with crushed stone and sand it forms *concrete*, which is used in foundation construction and for street-paving and road-building. It is also used in making artificial stone, terra-cotta trimmings for buildings, artificial-stone walks and floors, fence posts, and the like. It is being used more and more for making articles which were formerly made of wood or stone, and the entire walls of buildings are sometimes made of cement blocks or of concrete. Where greater strength is needed, iron rods or wire are embedded in the concrete before it sets, and this is called *reënforced concrete* (Fig. 188).

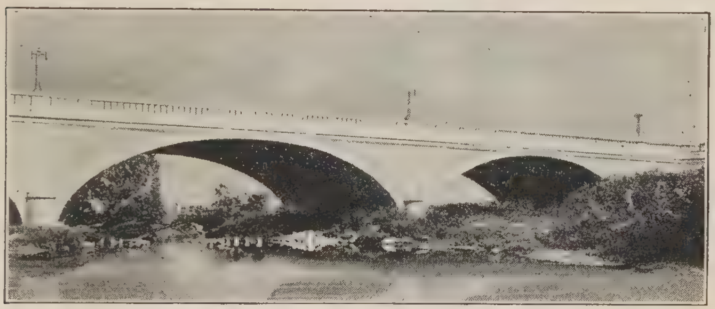


FIG. 188. A bridge built of reënforced concrete

CHAPTER SUMMARY IN QUESTION FORM

1. Name the four minerals that constitute the raw materials for the silicate industry.

2. Name the four metals whose silicates make up the larger part of the finished products of the silicate industry.

3. Supply the missing words: Glass is a mixture of ______. It is really an undercooled ______, although as rigid as a true ______. It is prepared by heating ______ with materials that contain the necessary ______.

4. Name (*a*) a glass article that is blown by machinery; (*b*) one that is blown into a revolving mold; (*c*) one that is formed into long cylinders, and then cut lengthwise and flattened into sheets; (*d*) one that is not blown but rolled, and then cut and polished.

5. What variety of glass is composed of a mixture of (*a*) silicates of sodium and calcium? (*b*) silicates and borates of sodium and aluminum with much free silica? (*c*) lead and other silicates?

6. To the presence of what metal is the color of (*a*) cheap bottle glass due? (*b*) blue glass? (*c*) purple glass? (*d*) ruby-red glass? (*e*) glass used in the tail-lights of automobiles?

7. What name is given to earth composed essentially of aluminum silicate and sand?

8. What is the difference between kaolin and clay?

9. (*a*) What physical properties have kaolin and clay that make them so useful? (*b*) The manufacture of what articles is based on these properties?

10. (*a*) Why is glass made from ordinary sand, green? (*b*) Why are ordinary bricks, red?

11. Supply the missing words: A mortar that has the property of hardening in water as well as air is called ______. It is a mixture of silicates, and is therefore similar to ______, but unlike it because it has in it more ______ and less ______ than ______.

THOUGHT QUESTIONS

1. Why not make glass from sand alone?

2. Why not make glass by heating sand with sodium carbonate?

3. Are bricks ever glazed?

4. Would you glaze (*a*) sewer pipe? (*b*) drainage tile?

FOR HONOR STUDENTS

1. Collect and exhibit to the class samples of the following substances used in the silicate industry: ordinary sand; pure sand; limestone; feldspar. Label the samples so as to show the composition of each.

2. Make a permanent collection of the finished clay products for your school.

3. Read one of the following chapters of "Chemistry in Industry," and report items of interest: (*a*) Chapter X in Volume I, entitled "Glass: One of Man's Blessings"; (*b*) Chapter VI in Volume II, entitled "Earthenware and Porcelain"; (*c*) Chapter XV in Volume II, entitled "Portland Cement."

CHAPTER XXXI

THE COLLOIDAL STATE

The Chemistry of Very Small Particles

437. *Introduction.* No one need be told that it is an easy matter to throw a book across a room, but everyone also knows that if the pages are torn out it will be impossible to throw them very far one by one. A piece of chalk will fall to the floor as quickly as will any other ordinary object; but if it is very finely *powdered,* it will take a long time for all the chalk dust to settle. It is evident that the *form* of a given weight of material has a great effect upon how it will act. Any other material in thin leaves or in fine dust will act like paper or chalk; so it is sometimes the *form* rather than the *material* that is important.

In a similar way, chemists have found that the *chemical conduct* of materials is often greatly modified when these materials are in the form of very fine powders, or droplets, or threads, or films; and often the properties depend more upon the fineness of division than upon the chemical composition of the material.

438. Colloidal state; colloidal dispersion. If coarse sand is shaken up with water it quickly settles when the shaking stops. The finer the sand, the more slowly it will settle. If we powder it fine enough and then stir it into water, it will not settle at all, for the particles will be so small that they will be kept in constant motion by collisions with the molecules of the water. If we could powder the sand into individual molecules and stir these into water, we should have a true solution.

Particles of one particular size are of great interest to chemists. *These are particles much too small to be seen by the most powerful ordinary microscope, yet made up of many thousand molecules.* Such particles suspended in a liquid (or in a gas) are called *colloidal dispersions,* and matter broken up to this degree of fineness is said to be in the *colloidal state.* Sometimes matter in this condition is called simply a *colloid,* but this is confusing, since it seems to indicate that certain substances are colloids and others are not; whereas *any* substance, under proper conditions, may be expected to get into the colloidal state just as it may be expected to get into solution, or into the dissolved state. *Colloid chemistry is the chemistry of very small particles, droplets, threads, and films.*

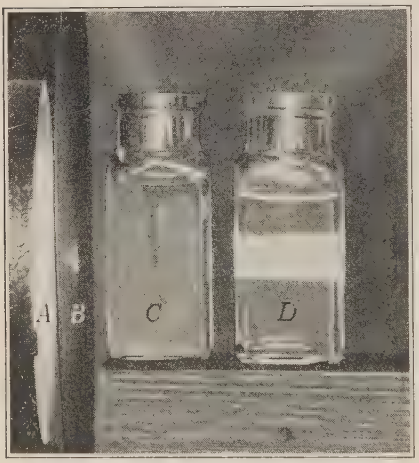


FIG. 189. The Tyndall cone

Light from the lantern *A* shines through a small hole in the screen *B*. Its path through pure water in *C* is not visible, but is very bright in the colloidal dispersion in *D*

The air in a quiet room always contains particles of colloidal size that are too small to be seen as objects by a microscope. But if the room is dark and a beam of sunshine enters through a small hole, these minute particles can be seen as bright, flashing points, or motes, dancing in the sunbeam. In like manner a colloidal suspension in a liquid that appears perfectly clear to the eye or to the microscope is seen to be full of moving particles when a strong beam of light shines through the liquid (Fig. 189).

This bright path of light through the liquid is known as the *Tyndall cone*, after the great English experimenter who described the experiment. A suitable apparatus for producing the Tyndall cone, together with a microscope for viewing the flashing points of light in the cone, is called an *ultramicroscope*. This instrument enables us to distinguish easily between a pure solution and a colloidal dispersion.

439. How colloidal dispersions are made. There are two general plans for making colloidal dispersions, each of which may be modified in many details:

1. An insoluble solid may actually be powdered to the necessary fineness and then stirred into the liquid (usually water). Special *colloid mills* are now sold for grinding materials into this fine form. Almost any sample of sand or ocean water shows traces of gold probably powdered to colloidal size by the natural grinding processes of nature. A colloidal dispersion of gold, silver, or platinum is easily prepared by forming an electric arc between wires of the metal dipped under water. The current tears off minute particles as a kind of smoke and disperses them through the water (Fig. 190).

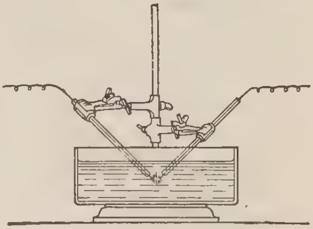


FIG. 190. The preparation of metallic colloids by sparking under water

2. We may bring about a reaction that ordinarily produces a precipitate, but under conditions such that the minute particles formed at first fail to gather together into particles large enough to settle as a precipitate. For example, we may add acid to a dilute solution of the salt known as sodium thiosulfate. No immediate precipitate of sulfur forms, but colloidal sulfur is present, as is evident from the white color. After a time some sulfur may precipitate, but most of it remains in suspension.

440. Properties of colloidal dispersions. Most of the properties of colloidal dispersions are due to the size of the particles rather than to the kind of matter composing them.

1. All colloidal particles are charged electrically, some kinds positively and some negatively; in an electrical field they act like the ions of a salt, moving to one or the other electrode.

2. Many colloidal dispersions are highly colored, but the color gives us little clue as to what is present. Colloidal gold may be red, blue, green, or violet, depending upon the size and uniformity of the particles. A little ferric chloride added to boiling water gives a deep-red colloidal iron hydroxide.

It takes very little of the colloidal substance to make an intense color. A few milligrams of gold will color a liter of water. A very little of the element selenium added to glass makes the intensely red glass of the automobile tail-light. Many colored glasses and glazes owe their color to colloidal material of various sorts, and many gems are colored in the same way. The blue of the sky and of deep mountain lakes is probably due to colloidal dust in the air and the water.

3. Since the colloidal particles are exceedingly small, they cannot be filtered out by any ordinary filter.

441. Coagulation of colloidal dispersions. It often happens that a colloidal dispersion is objectionable and we want to remove it or recover the colloidal material. We must then change the electrical or chemical conditions so that the very small particles will grow together into large clumps that will precipitate. We have found a number of ways to accomplish this:

1. A given colloid may be apt to remain suspended in an *alkaline* solution but to be precipitated in an *acid* solution; or it may be just the reverse. So the addition of a little acid or alkali is apt to cause the colloidal particles to precipitate, or *coagulate,* as it is called.

Thus, casein, an important colloidal substance in milk, coagulates to a curd when the milk becomes sour or acid in reaction. Rubber is coagulated from the sap of rubber trees by the addition of acetic acid. On the other hand, many metallic oxides are precipitated by alkalies.

2. Sometimes a concentrated salt solution will coagulate a colloidal dispersion. Thus, most river water carries much colloidal clay and organic matter. When it reaches the salt water of the ocean this matter is precipitated and builds up the great river deltas such as those of the Mississippi or the Nile. In every soap factory colloidal soap is separated from its solutions by the addition of common salt.

3. We have seen that all colloidal particles are electrically charged. It has been found that when two colloids of opposite charge are brought together, they mutually precipitate each other. Thus, in ordinary water purification the negative colloidal particles in river water are precipitated by the positive colloids supplied by alum or iron salts added for that purpose. The processes of dyeing and tanning depend upon this same principle.

442. Preserving and renewing colloidal dispersion. It frequently happens that in many industrial operations we want to preserve the colloidal state or bring a colloidal precipitate once more into dispersed condition. For many purposes the colloidal suspension of an insoluble solid is just as good as a true solution. In some cases we can use the original methods for preparing a colloidal dispersion; thus, by a process similar to grinding, graphite may be suspended in oil or water to make a very effective lubricant for machinery (oil dag and water dag). We may reverse the acidity or alkalinity that caused the coagulation; thus, antimony sulfide precipitated in acid solution may be dispersed again in an alkaline medium. We may filter the precipitate from the salt solution that produced precipitation and disperse it once more in pure water. If we bring together two colloids of the same electrical sign, each tends to hold the other in the colloidal state; thus, we add gum arabic to some kinds of inks to hold the colloidal black material in suspension. This is the chief reason for adding gums, dextrin, starch, and similar materials to many industrial and medicinal preparations.

443. Colloids and crystallization. It is an interesting fact that the presence of a colloidal material often tends to prevent distinct crystallization or at least to make the crystals very small and soft. Hence we put colloidal gelatin into ice cream, and gelatin, starch, dextrin, and similar materials in many candies and in electrolytic baths during electroplating, for in these processes we wish to avoid large or hard crystals. The colloidal materials in honey keep the concentrated sugar solution from crystallizing.

444. Adsorption. Sometimes a solid can be obtained in a very porous form that has a very large total surface in comparison with its weight. Activated charcoal (§ 160) is a solid of this kind, and it is estimated that 1 cc. of it has a surface of 1000 sq. m. Such materials (as well as colloidal particles whose surface is proportionally much greater) often have the property of attracting to their surfaces, or *adsorbing*, gases or dissolved substances. At room temperatures 1 cc. of activated charcoal will adsorb about 150 cc. of ammonia gas. It will also adsorb gasoline molecules from natural gas and give them up again when heated. In this way large quantities of gasoline are recovered (casing-head gasoline). *Fuller's earth* is a kind of finely divided clay that is used to adsorb the yellow coloring matter from cottonseed oil. This principle of adsorption is widely applied in chemical manufacturing.

445. Emulsions. If we pour together two liquids that do not mix, like oil and water, and shake the mixture violently, we get a milky-looking fluid called an *emulsion* (Fig. 191).

This consists of very minute drops of the one liquid dispersed through the other. If we let the emulsion of oil in water stand, it will very soon separate into the original liquids from which it was made. To make an emulsion of any kind *permanent* we must add a third colloidal substance insoluble in both of the liquids. This is called the *emulsifying agent.* It seems to form a little skin over the surface of the drops and prevents them from running together into big ones. *Milk* is an emulsion of butter fat in water, with *casein* as the emulsifying agent. When the milk turns sour the casein coagulates, and the butter fat is then easily collected into large lumps of butter. Most of our common disinfectants owe their properties to cresylic acid (§ 520) emulsified in water, with a small percentage of soap as the emulsifying agent. In *mayonnaise,* olive oil is emulsified in water (usually with a little vinegar added) by the colloidal yolk of egg, forming a stiff, almost jelly-like product. Fluids that form the webs of spiders and silkworms are secreted as emulsions which almost at once dry to form very fine filaments.

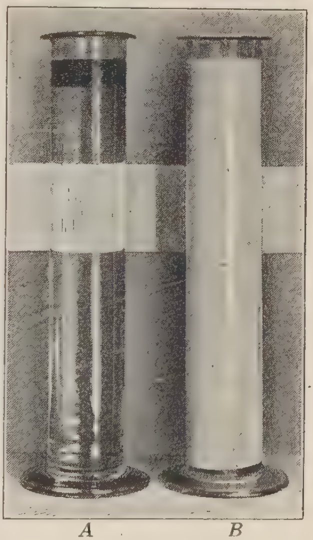


FIG. 191. Emulsions

When oil and water are shaken together, the oil soon separates on standing (*A*); if a little soap is added to the oil and water, and the mixture shaken, the emulsion becomes more permanent (*B*)

446. Jellies. Sometimes a colloidal substance tends to take the shape of very thin films rather than particles or filaments, and these films may form in such a way as to inclose the liquid, much as the walls of the honeycomb inclose the honey or the pores of a sponge hold water. When this happens the whole dispersion is likely to *set* to a more or less firm form called a *jelly* or a *gel*. Thus, if we add acid to a solution of sodium silicate, the dilute dispersion of silicic acid soon sets to a firm jelly. Casein sets to a jelly when coagulated (Fig. 220). In fruit jellies it is a constituent of the unripe fruit called *pectin* that serves to form the supporting structure. In gelatin or glue the jelly may be dried out to a very compact form, but when this is dissolved in hot water and cooled a jelly is once more obtained. Soap is a partially dried jelly; many minerals, such as agate, flint, and opal, are dry jellies; photographic films and many high explosives are jellies. Almost any sparingly soluble substance that does not crystallize too readily may be obtained in the form of a jelly. The so-called *solidified alcohol*, used largely at the present time, consists of a porous soap and alcohol, the soap acting as a sort of sponge to hold the alcohol. As yet we do not understand the conditions that lead to the formation of these jellies, and we obtain them largely by accident or by a cut-and-try process.

447. Smokes. Evidently we may have very fine particles suspended in the air rather than in water, and such a suspension is a *smoke*. It is often very hard to condense the particles of a smoke into solid form, and this fact is of enormous industrial importance. Many precious materials literally "go up in smoke" from the stacks of smelters; much zinc is lost as a smoke of zinc oxide in brass foundries; valuable potassium compounds are lost in the smoke of cement burners; and ordinary carbon smoke causes great losses to the individual but profit to the laundries.

All these smoke particles are electrically charged, and the American chemist Cottrell has devised a most effective process for the recovery of these particles by causing the smoke to move past metal plates and points charged electrically. The smoke particles lose their charge and then coagulate, much as a precipitate forms from a solution, and settle on the sides of the chimney (Fig. 192). The tails of comets are largely made up of particles of colloidal size.

448. Fogs and foams. Fogs consist of very fine droplets of liquid (usually water) suspended in air, so that they correspond to *emulsions*. Foams are gas bubbles dispersed through a liquid. Sometimes these minute gas bubbles are dispersed through what we should usually consider a solid, and often give to it a pure white color.

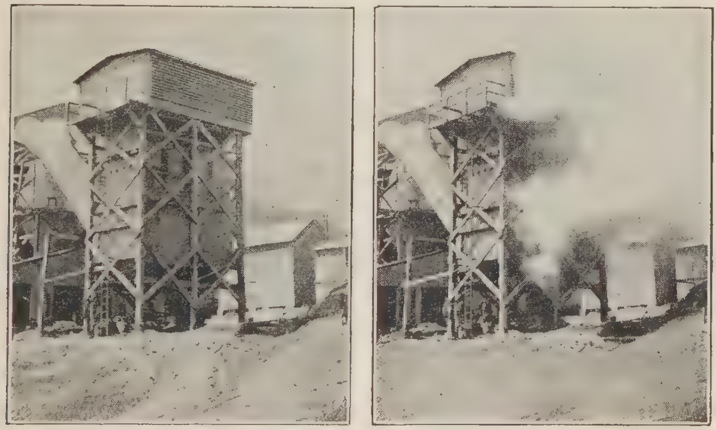


FIG. 192. View of a factory showing the effect of the Cottrell method for abating dust and smoke

At the left, a factory equipped with Cottrell apparatus; at the right, the same factory not equipped with Cottrell apparatus

CHAPTER SUMMARY IN QUESTION FORM

1. What term do we apply to particles suspended in a liquid, the particles being much too small to be seen through a microscope, yet made up of many thousands of molecules?

2. How can you tell such a liquid as is described in question 1 from a true solution?

3. Mention two ways in which matter can be obtained in this finely divided state.

4. In what way do colloidal particles resemble ions?

5. Should you say that the color of a colloidal dispersion depends essentially upon the size of the particles, the uniformity of the particles, the materials used, or the nature of the electrical charge?

6. What operation will remove precipitates from a liquid but will not remove colloidal particles?

7. Suppose you have a colloidal dispersion, and wish to precipitate (coagulate) the particles so as to remove them from the liquid. Mention three methods that you could try out for doing this.

8. Mention two industrial operations whose success depends on preserving the colloidal state.

9. Supply the missing words: Activated charcoal ______ gases. This property of charcoal makes possible the recovery of large amounts of ______ from natural gas.

10. Is milk (*a*) a solution? (*b*) a colloidal dispersion? (*c*) an emulsion?

11. What substance causes the colloidal dispersion that exists in fruit juices to form a jelly or *gel*?

12. What property of colloidal particles makes possible the Cottrell process for preventing smoke?

THOUGHT QUESTIONS

1. Crank-case oil and oil used in other machinery becomes very black; yet very little of the color is removed by filtration. How do you account for this?

2. Sugar is used in making jelly. Ordinarily the sugar does not crystallize out when the jelly forms, although an occasional glass is found with large crystals of sugar scattered through the jelly. Explain.

3. Fertile soils are essentially a kind of colloid jelly made up of clay and organic matter. When soluble salts such as ammonium sulfate and sodium nitrate are used as fertilizers, why are they not all dissolved and carried away by the first rain?

4. Can you explain why gravity, which causes large particles suspended in a liquid to settle, will not also cause small particles to settle?

5. From your knowledge of colloidal dispersions, give a reason for each of the following: (*a*) the formation of large soil deposits at the mouth of certain rivers that empty into the ocean; (*b*) the use of gums in the manufacture of some inks; (*c*) the use of gelatin in the manufacture of ice cream; (*d*) the use of the yolk of egg in making mayonnaise.

FOR HONOR STUDENTS

1. Arrange the necessary apparatus for showing the Tyndall cone, using an ordinary projection lantern or any other source of a strong beam of light. Test different liquids before the class, showing in this way which are true solutions and which are colloidal dispersions.

2. Read Chapter XX (entitled "Bubbles, Drops, Grains, and Films; Colloid Chemistry") in Foster's "Romance of Chemistry," and report some of the most interesting facts to the class.

CHAPTER XXXII

PETROLEUM AND THE COMPOUNDS THAT COMPOSE IT

I. Petroleum

449. ***Introduction.*** Chapter VI of this text bears the title "Water, the Most Important Liquid in the World." Next in importance among the naturally occurring liquids comes petroleum — a dark-colored mixture of various compounds, which is found in large quantities in many localities. It runs our automobiles (nearly twenty-five millions of them in the United States), lubricates our machinery, drives many of our ships and locomotives, flies our airplanes, plows our land and reaps our crops, heats and lights many of our homes, and in numberless other ways contributes to our welfare.

So far as is known, petroleum was first used in the United States by a druggist in Pittsburgh, who in 1849 collected some of the oil from a salt well, and sold it at the rate of 50 cents a half-pint bottle, as "A Natural Remedy — Celebrated for its wonderful curative properties." The fact that it would burn suggested its use as a fuel, and the first oil well was sunk in Pennsylvania, in 1859. From this date, the production of petroleum has increased steadily until now the United States produces yearly 900,000,000 barrels, or about $7\frac{1}{2}$ barrels for each inhabitant. Certainly we want to know something about this wonderful liquid.

450. The composition of petroleum; the hydrocarbons. Petroleum is obtained by sinking wells into the petroleum-bearing rock (Figs. 193, 194). The liquid obtained in this

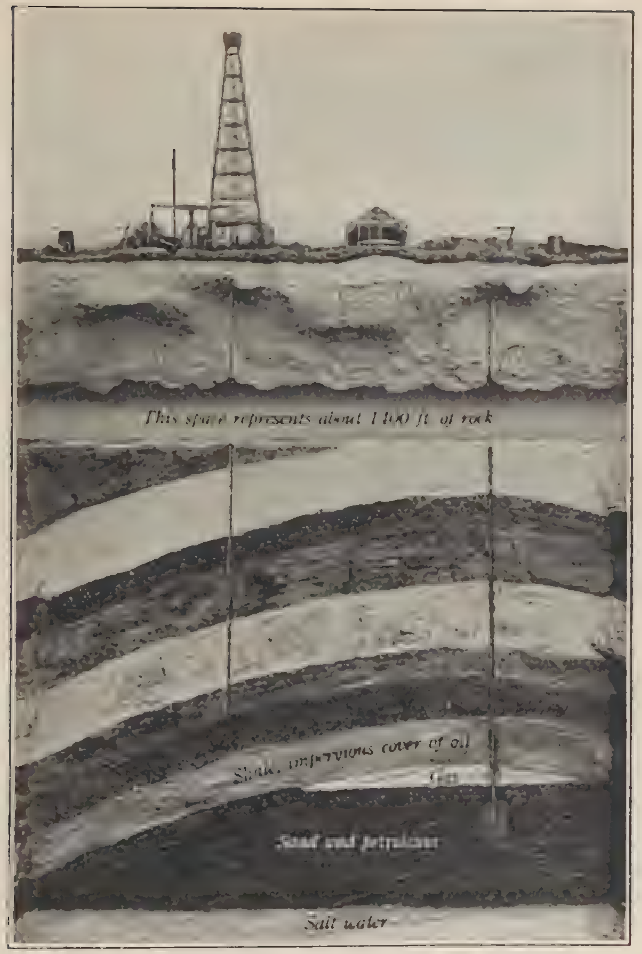

This space represents about 1400 ft. of rock
Shale, impervious cover of oil
Gas
Sand and petroleum
Salt water

FIG. 193. Typical structure of rocks in oil fields

Wells are sunk into the oil-bearing strata which occur at depths below the earth's surface varying from a few feet to 4000 ft. or more. At the left of the picture the shaft is shown as having reached nearly to the shale which forms an impervious cover over the oil-bearing rock. On the right the shaft is shown as having penetrated into the oil-bearing rock, so that the oil can be pumped to the surface. Often the oil will flow to the surface under its own pressure. (Courtesy of the Field Museum of Natural History)

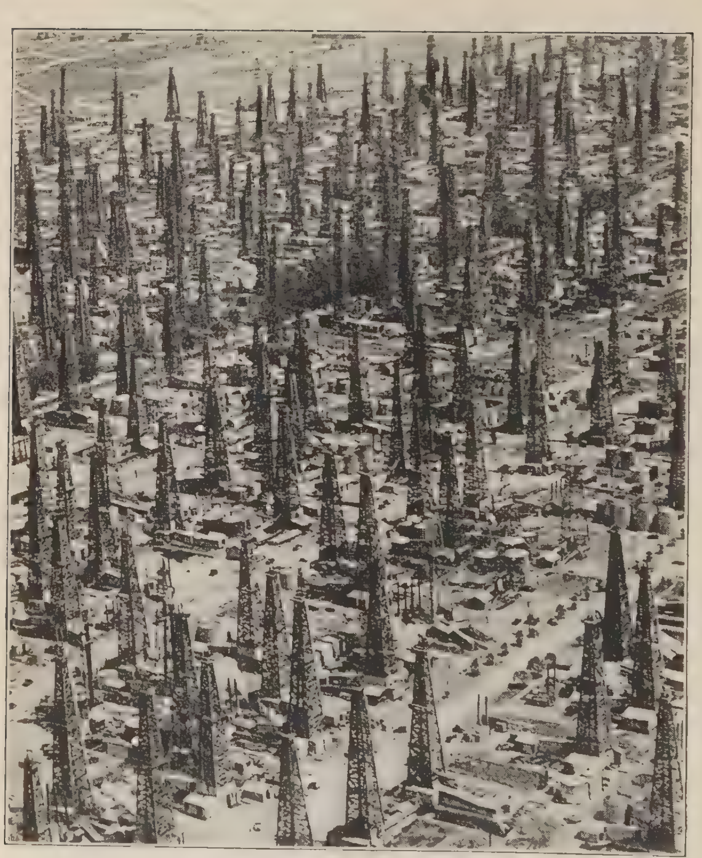


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FIG. 194. View in a typical oil field

A part of one of America's richest oil fields, namely, the one located at Signal Hill, near Long Beach, California. Derricks are as thick as trees in a forest. The oil is stored in the large tanks shown in the figure, or else piped directly to the refineries way is a complex mixture of many compounds, most of which are made up exclusively of carbon and hydrogen. *A compound composed of carbon and hydrogen only is called a hydrocarbon.* There are many hundreds of these hydrocarbons, and in order to simplify their study they are arranged in groups or series. The most extensive of these is known from its first or parent member as the *methane series.* In the following table are the names, formulas, and boiling points of some of the members of this series:

	Boiling Point		**Boiling Point**
Methane (CH_4)	−161.4°	Pentane (C_5H_{12})	+36.2°
Ethane (C_2H_6)	−88.3°	Hexane (C_6H_{14})	+69.0°
Propane (C_3H_8)	−44.5°	Heptane (C_7H_{16})	+98.4°
Butane (C_4H_{10})	+0.6°	Octane (C_8H_{18})	+124.6°

It will be seen that each member of this series differs from the one preceding it by the group of atoms CH_2, and that the boiling points gradually increase. All the members of this series are known up to the one having the formula $C_{28}H_{58}$.

The first four members of the series are gases at ordinary temperatures (see their boiling points). Those containing from 5 to 16 carbon atoms are liquids, the boiling points of which increase with the number of carbon atoms present; those containing more than 16 carbon atoms are solids. They are all insoluble in water, and when pure are colorless. They are not readily acted upon by other compounds; even strong acids and bases have little or no action upon them. *All of them are readily combustible,* however, especially the gaseous and volatile liquid members of the series. *When they are set on fire, the carbon burns to carbon dioxide and the hydrogen to water.*

451. The refining of petroleum. Petroleum consists of liquid hydrocarbons in which are dissolved both gaseous and solid hydrocarbons, together with many undesirable impurities. Before it can be used for most purposes it must be separated into fractions, each fraction being composed of a group of compounds boiling between certain limits. In this process the crude oil is heated in large iron stills (Fig. 195). The distillates which pass over between certain limits of temperature are kept separate. Of course the compounds of lowest boiling points distill over first, gradually followed by others in the general order of their boiling points.

The mixture passing over below about 200° is known as *naphtha*, which includes *gasoline*; that between 200° and 300° serves as a source of ordinary *kerosene*. Next comes over a fraction used as a *fuel oil*, and finally the paraffin distillate, from which are obtained *lubricating oils, vaseline*, and *paraffin*.

These different fractions are next stirred up first with sulfuric acid, then with a solution of sodium hydroxide, and finally with water, and then redistilled. This treatment removes most of the impurities present. *It is important to note that none of these products obtained from petroleum is a single compound; each one consists of a group of compounds boiling between certain limits of temperature.*

452. Naphthas; gasoline; benzine. Various grades of naphthas are known, the most important being ordinary *gasoline*. *Benzine* is a grade used in the paint industry and as a solvent. A low-boiling naphtha is used for cleaning fabrics (dry cleaning).

Gasoline is the most valuable of the products obtained from petroleum, and so every effort is made to obtain as large a percentage of it as possible from petroleum. To increase the percentage, the petroleum is distilled under pressure, which causes the heavier molecules (those of higher boiling points) to break down into molecules of lower boiling point which constitute gasoline. This process is known as the *cracking* of oils. Enormous amounts of gasoline are used, amounting in the United States to more than a hundred gallons for each inhabitant per year.

Because of the ease with which benzine and gasoline (these two names are often used interchangeably) burn and also because of the explosive character of their vapor when mixed with air, accidents often result from their use, especially when they are employed in our homes for cleaning fabrics. Recent statistics show that in the United States in a single year 1040 persons were burned to death and 3120 injured as a result of gasoline fires. It is obvious, therefore, that the greatest care should be exercised in handling gasoline.

453. Fractional distillation. The process of purifying a mixture such as petroleum is known as *fractional distillation.* In this process the mixture is heated, and in a general way the compounds distill over in the order of their boiling points. By repeating the process it is ordinarily possible to separate a mixture into the compounds present. In the refining of petroleum it is not necessary to effect such a sharp separation, but only to obtain a mixture of compounds which boil within certain limits.

II. Some Individual Hydrocarbons

454. General. It is important for us to study the properties of two of the hydrocarbons somewhat more in detail because they are so largely used for commercial purposes. These two are methane and acetylene.

455. Methane (CH_4). Pure methane is a colorless, odorless gas about half as heavy as air. It is commonly known as *marsh gas,* since it is formed in the mud of marshes and, in general, wherever organic matter decays or is heated in the absence of air. Bubbles of the gas are often noticed when the leaves on the bottom of a stagnant pool are stirred. It constitutes about 30 per cent of coal gas and from 90 per cent to 95 per cent of natural gas. Methane often collects in mines, and when mixed with air is called *fire damp*. *Such mixtures are very explosive* and are the cause of many terrible mine explosions (Fig. 76). When ignited, methane burns with a pale-blue flame. The flame is very hot, evolving 192,460 cal. for each gram-molecule of methane burned, as expressed in the equation

$$CH_4 + 2\ O_2 \longrightarrow CO_2 + 2\ H_2O + 192{,}460 \text{ cal.}$$

456. Halogen derivatives of methane. As a rule the hydrogen present in a hydrocarbon may be displaced by a halogen element, atom for atom. In this way there are formed from methane a number of derivatives, the most important of which are the following:

Chloroform ($CHCl_3$), a heavy colorless liquid boiling at 61°, is the well-known anæsthetic used in surgery. *Carbon tetrachloride* (CCl_4) resembles chloroform in appearance. It is a good solvent for fatty substances and it is used to remove grease spots from fabrics. It possesses the advantage over benzine of being noninflammable, but it is more expensive. Large quantities are used as a fire extinguisher (§ 170). *Iodoform* (CHI_3) is a yellow crystalline solid and is largely used as an antiseptic in the treatment of wounds.

457. Acetylene (C_2H_2). In addition to the hydrocarbons composing the methane series, many others are known. Among these is *acetylene*. This is a colorless gas and is easily obtained by the action of water on calcium carbide (CaC_2):

$$CaC_2 + 2\ H_2O \longrightarrow C_2H_2 + Ca(OH)_2$$

In this way the gas is prepared in large quantities for use as an illuminant and as a source of intense heat. When heated without air it decomposes, with evolution of a great deal of heat:

$$C_2H_2 \longrightarrow 2\ C + H_2 + 49{,}300 \text{ cal.}$$

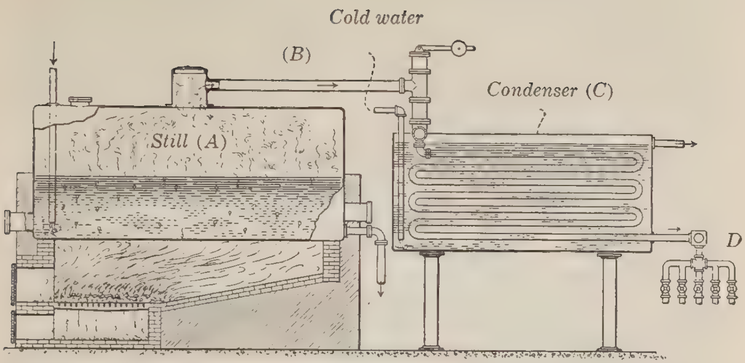

Cold water
(B)
Condenser (C)
Still (A)
D

FIG. 195. Diagram of apparatus used for distilling petroleum

The crude oil is run into the large still *A* and heated. The vapors pass off through *B* and are condensed in *C*. The resulting liquids are drawn off through *D*

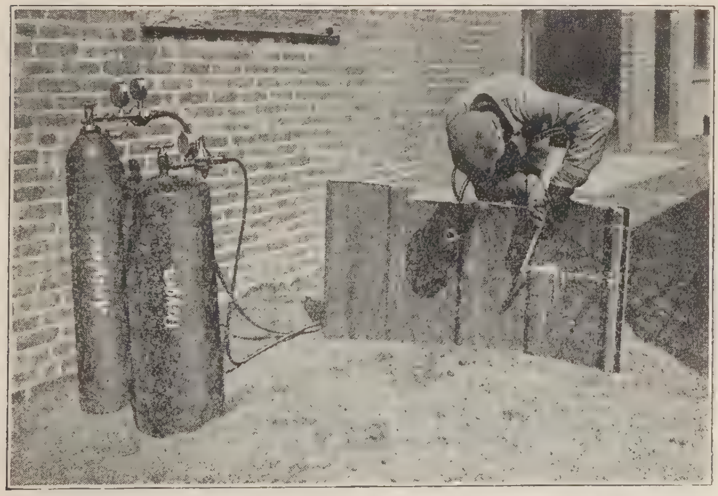


FIG. 196. Cutting an iron plate with the oxyacetylene blowpipe

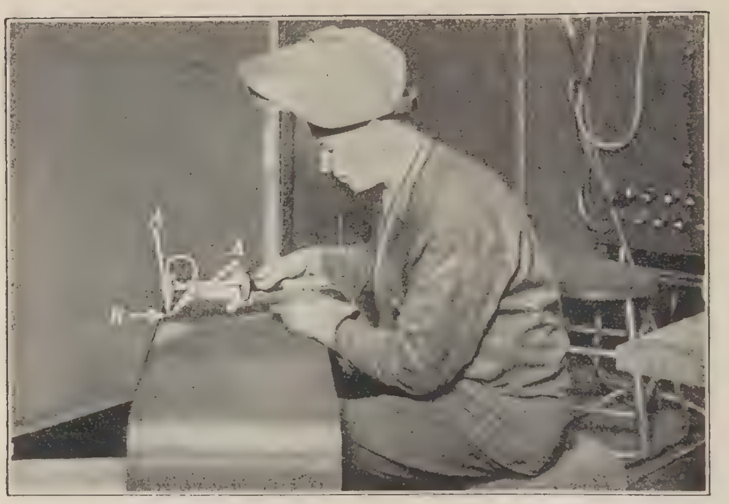


FIG. 197. The hydrogen-arc welding torch

An arc is formed at *B* at the ends of the tungsten electrodes *A*, *A*. Hydrogen is fed into this arc, is parted into atoms, and burns in oxygen

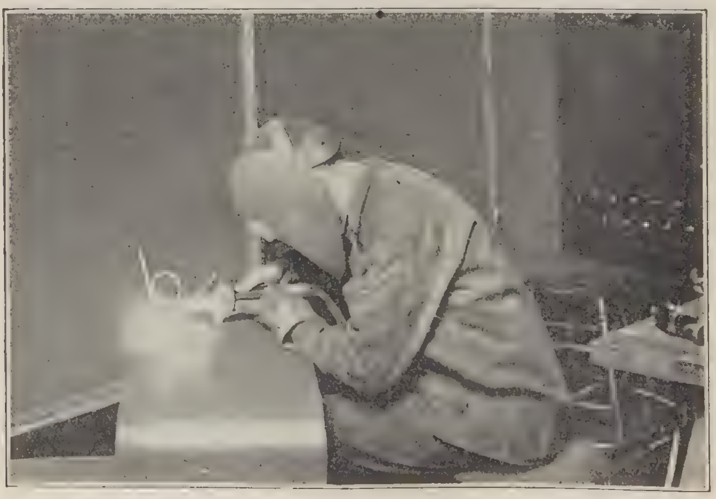


FIG. 198. The hydrogen-arc welding torch in operation

The operator protects his face and eyes by a hood, and applies the flame of burning hydrogen to the object to be welded

When compressed in cylinders acetylene is very explosive, since the heat liberated in compressing the gas is sufficient to start decomposition. It may, however, be stored safely in such cylinders, provided they are first filled with some porous material partially saturated with acetone (a liquid obtained by the destructive distillation of wood (§ 159, 2)). Under pressure a large quantity of the gas dissolves in the acetone. In this form acetylene is now a common article of commerce.

Under ordinary conditions acetylene burns with a smoky flame, but with a proper admixture of air it burns with a brilliant white light. The flame is very hot, because to the heat of combustion there is added the heat of decomposition, as expressed in the equation above. The complete equation for the combustion of acetylene is

$$2\,C_2H_2 + 5\,O_2 \longrightarrow 4\,CO_2 + 2\,H_2O + 2 \times 302{,}330 \text{ cal.}$$

458. Uses of acetylene. Acetylene has two important commercial uses: (1) As an illuminant it is used where electric lights are not available. (2) Its chief use, however, is as a source of intense heat. For this purpose the acetylene is burned with pure oxygen in an apparatus known as the *oxyacetylene blowpipe* (Fig. 196), which is very much like the oxyhydrogen blowpipe in principle.

459. Atomic hydrogen flames. In addition to the use of the oxyacetylene blowpipe, another method has been developed recently by the American chemist Langmuir (Fig. 162) for the production of the high temperatures necessary for the welding of metals. Langmuir found that when a current of hydrogen is passed through an electric arc produced between electrodes made of tungsten (the metal used in our electric-light filaments), the heat of the arc is sufficient to decompose the hydrogen molecules into atoms. As these atoms leave the electrode they immediately recombine to form molecules, generating a large amount of heat in the process. This heat, together with the heat of combustion of the hydrogen, is more intense than that produced by the oxyacetylene blowpipe. The apparatus for producing the flame is known as the *hydrogen-arc welding torch.* Its construction and the method of using it are shown in Figs. 197, 198.

460. Some problems. Many important problems are connected with the combustion of hydrocarbons. For example, suppose we wish to know what volume of oxygen would be required to burn 1000 cu. ft. of natural gas, on the supposition that it is pure methane; also what volume of carbon dioxide would be formed. Since methane, oxygen, and carbon dioxide are all gases, such a problem can easily be solved by applying the principle of Avogadro's law, as explained in the solution of similar problems in § 173. The steps are as follows:

$$\begin{array}{rr@{\;}l} & CH_4 + 2\,O_2 \longrightarrow & CO_2 + 2\,H_2O \\ & \text{1 molecule} + \text{2 molecules} \longrightarrow & \text{1 molecule} \\ & \text{1 volume} + \text{2 volumes} \longrightarrow & \text{1 volume} \\ \text{Hence} & \text{1000 cu. ft.} + \text{2000 cu. ft.} \longrightarrow & \text{1000 cu. ft.} \end{array}$$

CHAPTER SUMMARY IN QUESTION FORM

1. Supply the missing words: Compounds composed of carbon and hydrogen only are called ______. There are many ______ of these, and to simplify their study they are arranged in series, the most important of which is known as the ______ series, because the name of its first member is ______.

2. What relation exists between the boiling points of the members of the series referred to in question 1 and the number of carbon atoms present?

3. Give the names and formulas of the two products of complete combustion of each member of the series.

4. Which of the following statements is correct? Petroleum is composed of (*a*) a single liquid compound; (*b*) a mixture of liquid compounds; (*c*) a mixture of liquid compounds in which are dissolved both gaseous and solid compounds.

5. What name is given to the process of separating petroleum into several parts by distilling it and collecting the fractions that boil between certain limits of temperature?

6. Give the order in which the following products distill over in the process of refining petroleum: (*a*) fuel oil; (*b*) vaseline; (*c*) gasoline; (*d*) paraffin; (*e*) kerosene; (*f*) lubricating oils.

7. Name three compounds used in the purification of the above products.

8. (*a*) Name the most valuable petroleum product; (*b*) also name the process by which the amount of this product obtained from petroleum is greatly increased.

9. (*a*) What is the common name of methane? (*b*) How is it formed in nature? (*c*) What two useful gases contain it? (*d*) What name is given to a mixture of methane and air in mines? (*e*) Write the equation for its complete combustion.

10. Complete the following table relating to three important halogen derivatives of methane:

NAME	FORMULA	PHYSICAL STATE AND COLOR	USE
1.			
2.			
3.			

11. Write the equation for the reaction of water with calcium carbide.

12. Show by two equations why the heat of combustion of acetylene is so great.

13. What name is given to the process of heating two pieces of metal to their melting points and so effecting their fusion?

14. Give (*a*) the name of a compound and (*b*) the name of the apparatus used with that compound for producing the heat necessary for carrying out the above process.

15. (*a*) Substitute the word "element" for the word "compound," in question 14, and then answer the question. (*b*) Why is the heat produced in this case so very intense?

THOUGHT QUESTIONS

1. Mention the properties of gasoline that (*a*) make it useful in our homes; (*b*) make it dangerous.

2. Explain why hydrogen, oxygen, chlorine, carbon dioxide, and many other gases can be compressed in empty steel cylinders with safety, while acetylene cannot.

3. The flame of a lighted splint is extinguished when quickly plunged into kerosene. Do you think the same would be true of gasoline?

4. How do you account for the formation of carbon monoxide in a gasoline engine?

5. Write the equation for the complete combustion of acetylene. By inspection of the equation, tell (*a*) in what proportions by volume acetylene and oxygen will combine; (*b*) also the proportions of each of these to the volume of the carbon dioxide formed.

6. A certain stove burns 300 cu. ft. of natural gas daily. Assuming that the gas is pure methane, (*a*) what volume of oxygen is required for the complete combustion of the gas? (*b*) what volume of carbon dioxide is formed?

7. A given volume of hydrogen burns in the air with a very hot flame. How can the intensity of the heat be increased without increasing the pressure?

8. Some petroleum contains sulfur compounds. Give reasons why these must be removed.

FOR HONOR STUDENTS

1. Write a theme on the subject "The Uses of Petroleum and of the Products obtained from it."

2. Collect a set of samples of petroleum products for your school.

3. Read Chapter XVII ("The Petroleum Industry") in Volume I of "Chemistry in Industry," and report interesting facts to the class.

CHAPTER XXXIII

SOME FUELS AND RELATED TOPICS

461. *Historical.* Naturally, wood was the first fuel to be used; then came charcoal prepared from wood (§ 159, 2), which proved useful not only as a fuel but also as a reducing agent in obtaining metals from their ores. Then it was found that certain black stones (coal) would make a hot fire. The coal smoke proved objectionable in the larger cities, and as far back as the thirteenth century the use of coal was forbidden in London, England; later Queen Elizabeth prohibited the burning of coal in London while Parliament was in session, because the "health of the knights might suffer during their abode in the Metropolis." The advantage of coal soon overcame all objections to its use, and it is only in recent years that attention has again been called to the "smoke nuisance." The latest fuels to come into use are (1) petroleum and the fuel oils obtained from it and (2) the various fuel gases.

Solid and Liquid Fuels

462. General discussion. The use of coal, coke, and charcoal as fuels has been discussed in Chapter XI. Wood consists chiefly of compounds of carbon, hydrogen, and oxygen. When it burns, the carbon and hydrogen form carbon dioxide and water respectively.

Petroleum and certain oils derived from it are coming into large uses, especially in engines used for propelling ships and railway trains. The oil is sprayed into the furnace or fire boxes by compressed air. When ignited, the carbon and hydrogen in the oils burn to carbon dioxide and water.

Gaseous Fuels

463. Kinds of fuel gases. The most important of the fuel gases are (1) coal gas, (2) water gas, (3) producer gas, and (4) natural gas. We will now study briefly each of these.

464. Coal gas. It has been known for several centuries that when soft (bituminous) coal is heated out of contact with air, combustible gases are formed; indeed, gas prepared in this way has been used for street-lighting in a few of the larger cities both in England and in the United States for more than one hundred years.

The changes that take place when soft coal is heated in retorts out of contact with air result in the formation not only of those gases which constitute coal gas, but also of *ammonia* (§ 283, 2, (b)) and a thick tarry mass known as *coal tar*, which serves as the source of many useful compounds, as will be explained later. All these compounds, being vaporized by the heat, are conducted away, leaving the nonvolatile coke in the retort. In the manufacture of coal gas, then, we obtain not only the gas itself, but also coke, ammonia, and coal tar. The more important steps in the process are given in Fig. 199.

465. The by-product coke ovens. The coke obtained in the manufacture of coal gas is a very important product, useful not only as a fuel but especially as a reducing agent in obtaining metals, like iron, from their ores. The quantity of coke obtained in the manufacture of coal gas has never been sufficient to meet the demand. Much of the additional coke required has been made by heating the coal in *beehive ovens* — so named because of their shape. This was a very wasteful method, since all the by-products (coal gas, ammonia, and coal tar) escaped into the air. This wasteful process has now given way almost entirely to another in which coal is heated in the *by-product coke oven* (Fig. 200), which makes it possible to save all the products formed.

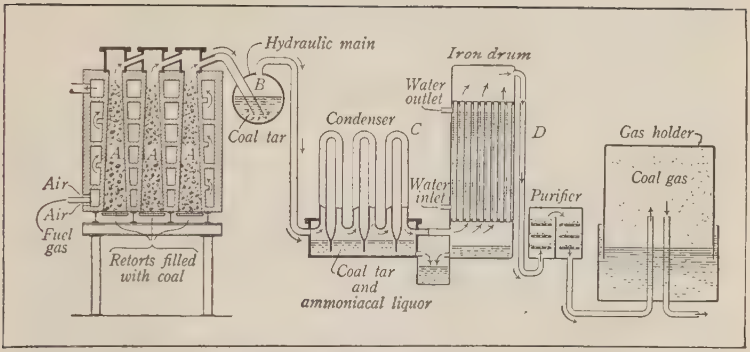


FIG. 199. Diagram showing the essential parts of the apparatus used in the manufacture of coal gas

The coal is introduced into rows of closed retorts, A, A, A, and heated. A delivery pipe leads from the top of each of the retorts into a large pipe B (known as the *hydraulic main*). The application of heat causes the coal to undergo complex changes which result in the formation of a large number of compounds. These compounds escape through the delivery pipe into the hydraulic main. The temperature being reduced, some of the products that are solid or liquid at ordinary temperatures condense in the hydraulic main in the form of a dark liquid known as *coal tar*. The gases then pass on into the condenser C, in which the products are cooled to such an extent that the remaining tar is deposited. Along with the tar there is condensed a liquid (chiefly water) containing ammonia in solution and known as *ammoniacal liquor*. The gas is then led into a large iron drum D, fitted with copper tubes, through which the gas passes. The tubes are kept cool by running water, and further condensation of vapors takes place in the tubes. From the drum D the gas passes into the purifier, where it comes into contact with lime or iron oxide, which removes any sulfur compounds present; from this it enters the large gas holder, from which it is distributed to consumers. The great bulk of the carbon remains in the retort as *coke* and as *retort carbon*. The yield of gas, tar, and soluble materials depends upon many factors, such as the composition of the coal, the temperature employed, and the rate of heating. One ton of good gas coal yields approximately 10,000 cu. ft. of gas, 1400 lb. of coke, 120 lb. of tar, and 20 gal. of ammoniacal liquor

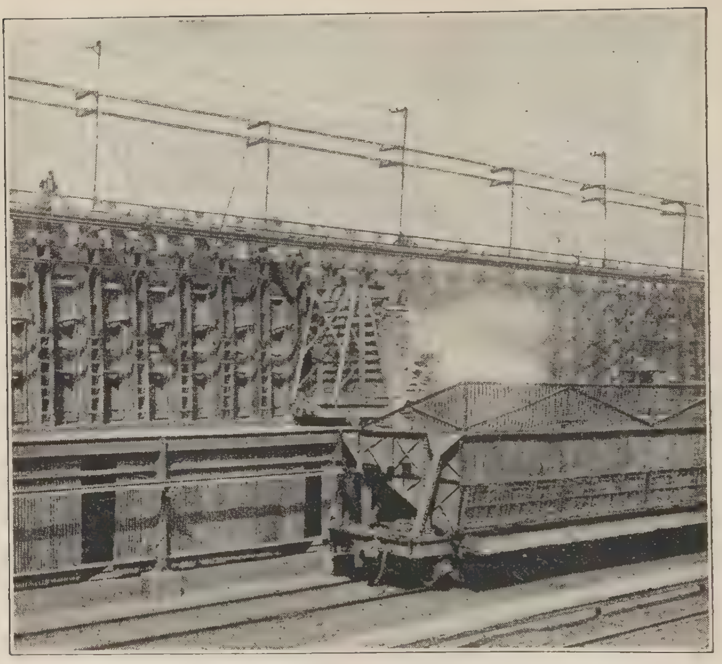


FIG. 200. View of a portion of a large by-product coking plant

The plant consists primarily of a number of narrow upright ovens placed side by side but separated by combustion chambers so as to admit of heating the coal with which the ovens are filled. Sometimes a portion of the gas generated in the process is used as a fuel for coking the coal; more often this is saved and the much cheaper *producer gas* (§ 467) used in its place. The hot flame of the burning gas strikes against the bottom and sides of the ovens. The coal tar and the ammonia are separated and collected as in the manufacture of coal gas; indeed, the by-product oven is a large coal-gas plant. When the process is complete, each oven is pushed forward and the coke dropped into a car, as shown in the figure. The by-product ovens are rapidly displacing the older beehive type. Of the nearly 50,000,000 tons of coke produced annually in the United States, more than three fourths is produced in the by-product ovens. Over 80 per cent of the output of coke is used in reducing iron from its ores

466. Water gas. Water gas is essentially a mixture of carbon monoxide and hydrogen. It is made by passing steam over very hot anthracite coal or coke, when the reaction shown in the following equation takes place:

$$C + H_2O \longrightarrow CO + H_2$$

The coal is burned in a draft of air until it is very hot. The air is then shut off and the steam turned on. The temperature gradually falls because the reaction absorbs heat, and when it reaches about 1000° the steam is cut off and the air supply renewed.

Water gas is effective as a fuel, since both carbon monoxide and hydrogen burn with very hot flames.

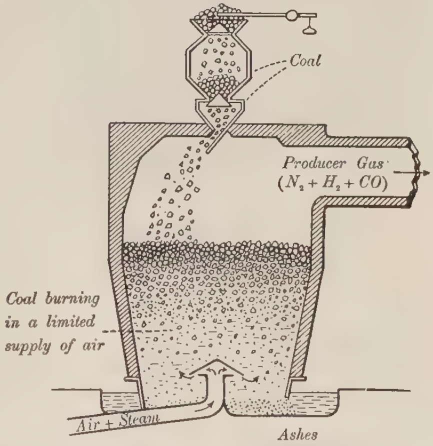


FIG. 201. Diagram illustrating the manufacture of producer gas

467. Producer gas. Producer gas is used in connection with many metallurgical furnace operations and also as a fuel for gas engines. It is made by burning coal under such conditions that the product of combustion is largely carbon monoxide (Fig. 201). Very often a little steam is admitted with the air, and this, on passing through the hot bed of coals, is reduced as in the preparation of water gas. Made in this way, producer gas is composed mainly of carbon monoxide, hydrogen, and nitrogen. It can be made from coal of a poor quality, even from lignite, and as gas engines run well with this gas, it furnishes the most economical method for utilizing low-grade coal for power.

468. Natural gas. In many regions of the United States, as well as in other countries, natural gas is obtained from wells drilled into a rock stratum holding the gas. While it is variable in composition, it consists largely of methane (CH_4), many samples containing as much as 95 per cent of this compound. It burns with intense heat and is an ideal fuel.

469. Comparative composition of fuel gases. In the table below are given the average results of the analyses of many samples of the different fuel gases. Since the composition of different samples of the same kind of gas varies considerably, the values must be taken as approximate only.

AVERAGE COMPOSITION OF DIFFERENT FUEL GASES

CONSTITUENT	OHIO NATURAL GAS	COAL GAS	WATER GAS	PRODUCER GAS
H_2	0.9	41.3	52.88	10.90
CH_4	89.5	43.6	2.16	
C_6H_6	9.3			
CO	0.4	6.4	36.80	20.10
CO_2	0.3	2.0	3.47	8.50
N_2	0.2	1.2	4.69	59.90
O_2	0.0	0.3		
Other hydrocarbons	0.3	5.4		0.60
Heat values in calories per cubic meter	8120	5333	2738	1402

470. Heat values of fuels. The various materials used as fuels differ much in the heat which they give out when burned. While many other factors are concerned in the value of a fuel, the chief one is its heat of combustion. In discussing a fuel gas, it is customary to give the number of calories of heat evolved in the combustion of a certain volume of the gas, such as one cubic meter (see above table). With solids, on the other hand, the heat value is generally expressed in terms of the *calorific value* of the fuel, which is *the heat evolved in the combustion of one gram of the fuel.*

In large contracts the price paid for a fuel is usually based on its calorific value as well as on its adaptability to the use to which it is to be put. The calorific value of, say, coal is determined by burning a definite weight of the sample in an air-tight metal cylinder filled with oxygen and surrounded by water. The heat evolved is absorbed by the water, and the increase in the temperature of the water is noted. The following table gives some average values for a few common solid fuels:

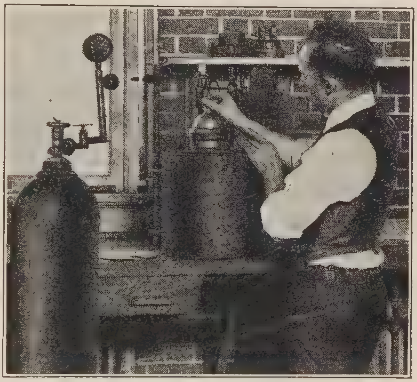


FIG. 202. Determining the calorific value of coal

CALORIFIC VALUE OF SOME SOLID FUELS

Wood (air-dried)	about 3800–4000 cal.
Bituminous coal (Pennsylvania), 35% volatile matter, 6% ash	about 8300 cal.
Bituminous coal (Pocahontas), 18% volatile matter, 6% ash	about 8700 cal.
Anthracite coal, 12% ash	about 7300 cal.
Coke, 10% ash	about 7300 cal.

471. Smoke-prevention. Studies made in recent years in some of our large cities call attention to the great loss both of money and of health by the pollution of the air in these cities with smoke. It is estimated that the loss of money amounts to more than $10 annually for each inhabitant, and this takes no account of the very serious effect upon health. A very important question is, then, How can this loss be avoided?

Since the main products of the combustion of fuels are carbon dioxide and water vapor, both of which are colorless compounds, it follows that if the combustion is complete no smoke will be formed. Unfortunately, in the way coal is burned in most of our homes and factories the combustion is not complete, and large amounts of finely divided carbon escape into the air. We can prevent smoke by securing complete combustion of the fuel. The necessary conditions for doing this are as follows: (1) a sufficient supply of air; (2) thorough mixing of the air with the combustible gases produced from the fuel; (3) a temperature high enough to maintain active combustion. Many "smoke-consuming" furnaces are now made, which claim to be constructed so as to secure complete combustion.

Soft coal, the most common fuel, is the chief smoke-producer. Moreover, in burning it we lose the important products coal tar and ammonia (§ 464). It seems probable that before long we shall stop using soft coal directly as a fuel, but shall first heat it in a by-product coke oven (§ 465) and use the resulting gas and coke as fuel. In this way not only would the coal tar and ammonia be saved, but the smoke problem would be solved, for coal gas and coke burn with little or no smoke.

Flames and Explosive Mixtures

472. Conditions necessary for flames. When the substance undergoing combustion remains solid at the temperature produced by combustion, light may be given off but there is no flame. Thus, iron wire burning in oxygen throws off a shower of sparks, but no flame is seen. When, however, both of the substances involved are gases or vapors *at the temperature reached in combustion,* the act of union is accompanied by a flame. Many solids (and liquids), such as a candle, burn with a flame, but this is because the heat of combustion first melts the solid, then vaporizes the liquid, and *the flame is the result of the union of this vapor with the oxygen* of the air. That the interior of a candle flame is composed of combustible vapor can be proved by holding one end of a glass tube in the flame as shown in Fig. 203. Some of the vapor escapes through the tube and may be ignited at the upper end of the tube.

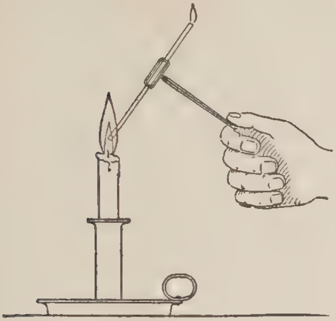


FIG. 203. Method of proving that the interior of a candle flame contains combustible vapors

473. Structure of a flame. When carbon monoxide or hydrogen burns in oxygen, but one reaction takes place, and as a result the flame is very simple in structure. It consists of a colorless inner cone of unburned gas and an outer cone in which the union between the gas and the oxygen is taking place. It thus follows that the outer cone is the hot part of the flame.

The flames produced by the combustion of hydrocarbons such as are present in coal gas and natural gas or of mixtures of hydrocarbons with related compounds, as in candles, are much more complex because several consecutive reactions take place. For example, in the candle flame (Fig. 204) there are, broadly speaking, three cones: (1) the inner cone *A*, composed of combustible vapors; (2) an intermediate cone *B*, in which these vapors are decomposed by the heat and a small quantity of carbon is set free which, being heated to incandescence, renders the flame luminous; and (3) an almost invisible narrow outer cone, or film, *C*, in which the hydrogen and carbon are burned to water and carbon dioxide respectively.

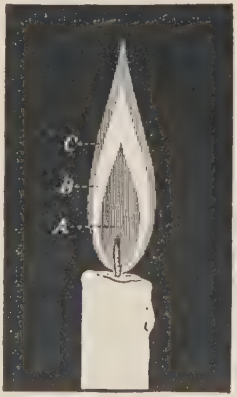


FIG. 204. The cones of a candle flame

474. Bunsen burners. In the ordinary Bunsen burner used in chemical laboratories and in similar burners used in gas stoves and ranges (Fig. 205), the gas is mixed with a certain percentage of air before it is burned. This is accomplished by having an opening (mixer) in the base of the burner (*A*, Fig. 205) into which the air is drawn by the flow of the gas. If the mixer is adjusted properly so that just the right amount of air is admitted, the flame is colorless. Such a flame possesses an advantage in that no carbon is deposited from it. It is well adapted, therefore, for gas ranges, since the bottom of the cooking vessels will be kept free from carbon. It may also be used for illuminating purposes, by hanging about the flame a so-called gas mantle, which is composed of a mixture of 99 per cent of thorium oxide and 1 per cent of cerium oxide. The flame heats this mixture to incandescence, and it glows with a brilliant light. These mantles have been largely used, but the electric light is gradually replacing all other forms of illumination.

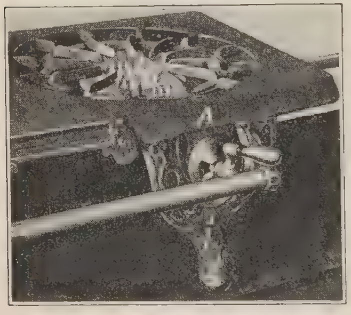


FIG. 205. A typical gas-burner

475. Oxidizing and reducing flames. The tip of the flame of a candle or of a Bunsen burner is very hot and air is abundant, so that a substance heated in this part of the flame tends to be oxidized; accordingly we call this part of the flame the *oxidizing flame.* The tip of the luminous cone (*B*, Fig. 204), on the other hand, contains the highly heated reducing gases hydrogen and carbon monoxide, and this part of the flame is called the *reducing flame.* Many metallic oxides, such as lead oxide, when heated in the reducing flame are reduced to metals.

We can sometimes gain rapid information as to what a substance is by trying the effect of the oxidizing and reducing flames upon it. This is easily done by using a mouth blowpipe as shown in Fig. 206. The blowpipe is a metal tube bent at one end and drawn out to a fine point. If the end of the tube is placed just at the edge of a small flame and a current of air is forced through the tube, the flame is bent at an angle, as shown in the figure. The tip of the flame is the oxidizing flame, the interior is the reducing flame. The substance to be tested is placed in a cavity on a piece of charcoal and held so that the desired part of the flame strikes it.

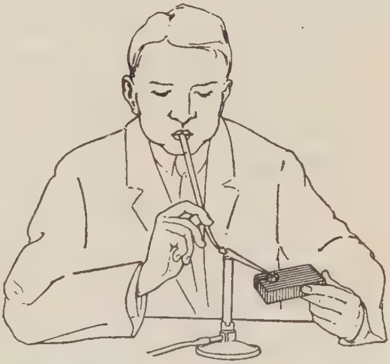


FIG. 206. Heating a metal in the oxidizing flame

476. Explosions and explosive mixtures. We often read of some disastrous explosion caused by the escape of fuel gas in a house. It is of interest to inquire into the cause of explosions and to learn the reason for their terrific power. *An explosion is due to a sudden chemical reaction in which the volume of the gases formed in the reaction is much larger than that of the reacting substances*; hence if the reacting substances are confined, as in a room or house, something must give way. Moreover, the greater the difference in this change in volume in a rapid reaction, the more violent will be the explosion. Often this increase in volume is due entirely to the heat evolved in the reaction (Charles's law, § 69).

But another question also arises. Suppose we are cooking with a gas range. It is probable that every time we light the gas a little of it escapes into the room, but no explosion takes place. Just how much of the gas can be present in the air of the room before it forms an explosive mixture? Experiments have proved that there is no danger of an explosion unless the mixture of air and gas falls between certain limits in percentage composition, and that these limits are perfectly definite for each kind of fuel gas. For natural gas (methane) the limits are 5 and 14; that is, natural gas escaping into the air of a room will not form an explosive mixture until the gas reaches 5 per cent by volume of the mixture; moreover, the mixture will cease to be explosive if the amount of gas present exceeds 14 per cent. For coal gas the limits are 6 and 29, and for acetylene the limits are 2.5 and 73.

477. Mine explosions. Some mine explosions are due to the presence of finely divided carbon in the air of the mine; others are due to the presence of methane in sufficient percentages to form an explosive mixture (§ 455). Such mixtures will not explode, however, unless the gases are heated to their ignition point; but a flame, or even a spark, is sufficient to cause the explosion. Formerly the miners used an open-flame oil lamp, and this would ignite an explosive mixture of gases. In 1815 the English chemist Sir Humphry Davy (Fig. 110) invented a miner's lamp in which the usual chimney of a lantern is replaced by a wire gauze (Fig. 207). A flame starting at the wick is so cooled by the wire gauze that ignition ceases and the flame is confined to the interior of the lamp (Fig. 209). The principle may be demonstrated by holding a wire gauze horizontally a couple of inches above a Bunsen burner (Fig. 208). If the gas is turned on and lighted above the gauze, the flame rests upon the gauze but does not pass below it.

478. Carburetors. The carburetors used in automobiles are simply devices for vaporizing the gasoline and obtaining an explosive mixture of the resulting vapor and air. This mixture is then led into the cylinders, and exploded

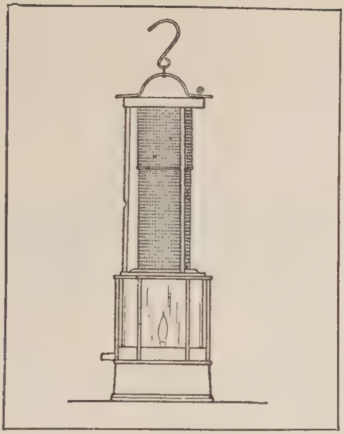


FIG. 207. The miner's safety lamp invented by Davy

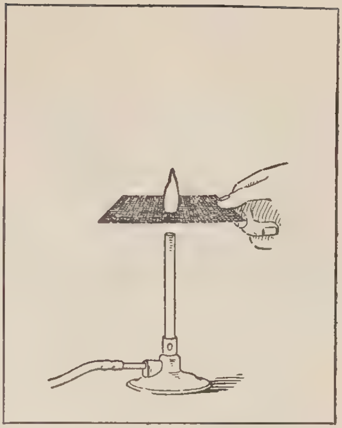


FIG. 208. Experiment illustrating principle of safety lamp

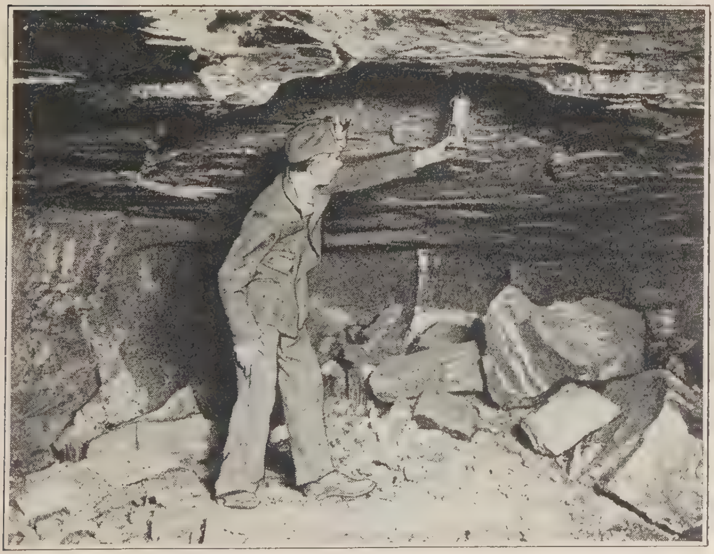


FIG. 209. Testing for pockets of explosive gas mixtures in a mine

A series of small explosions within the safety lamp gives warning of the presence of a dangerous explosive mixture

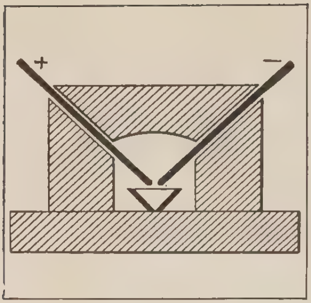


FIG. 210. An electric arc furnace

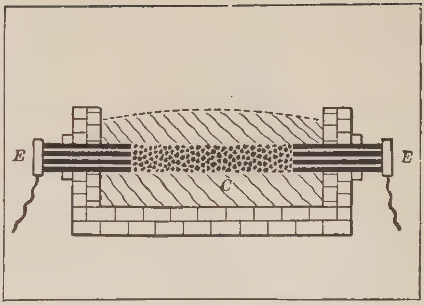


FIG. 211. An electric resistance furnace

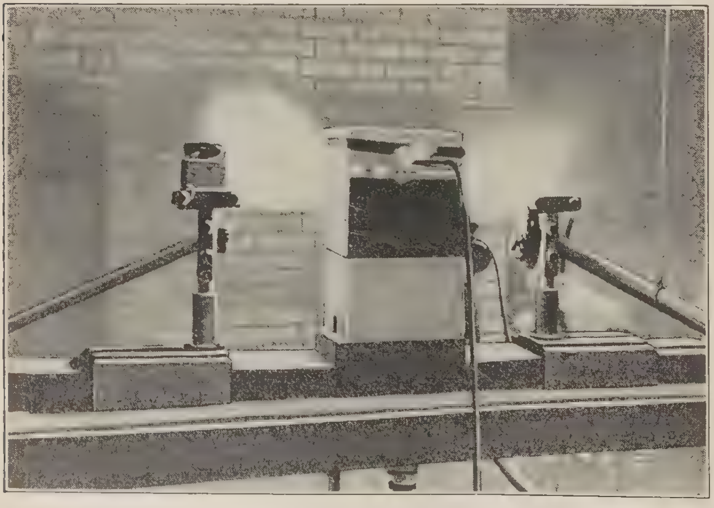


FIG. 212. View of an electric furnace used by Moissan, who was one of the first scientists to experiment with reactions at high temperatures

From Duncan's "Chemistry of Commerce"

by a spark. The principle involved in the construction of carburetors is shown in Fig. 213.

As was pointed out in the description of mine explosions, finely divided carbon floating in air forms an explosive mixture. Experiments are being conducted to see if such a mixture cannot be used as a fuel in gas engines.

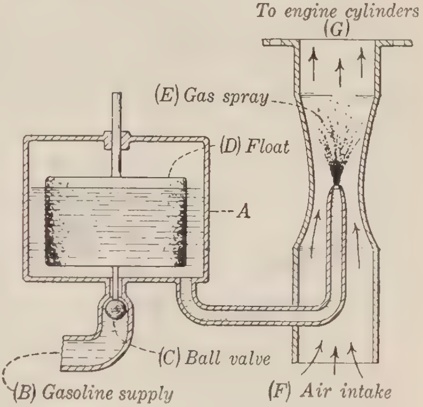


FIG. 213. Diagram of an automobile carburetor

By keeping gasoline at constant level in A, it issues as a fine spray from the jet E, and forms an explosive mixture with air drawn in at F. This mixture passes through G to the cylinders of the engine, where it is exploded by a spark

Electric Furnaces

479. The electric furnace. In recent years electric furnaces (Fig. 212) have come into wide use in operations requiring a very high temperature. Temperatures as high as 3500° can easily be reached. These furnaces are constructed on one of two general principles.

1. ***Arc furnaces.*** In the one type the source of heat is an electric arc formed between carbon electrodes separated a little from each other, as shown in Fig. 210. The substance to be heated is placed in a vessel, usually a graphite crucible, just below the arc.

2. ***Resistance furnaces.*** In the other type of furnace the heat is generated by the resistance offered to the current in its passage through the furnace. In its simplest form it may be represented by Fig. 211. The material to be heated, C, is placed between the ends of the electrodes E, E. The resistance offered to the passage of the current through this material generates the heat.

CHAPTER SUMMARY IN QUESTION FORM

1. Name a (*a*) solid fuel; (*b*) liquid fuel; (*c*) gaseous fuel.

2. Name four important products formed in the destructive distillation of coal.

3. What products, wasted when coke was made in the beehive ovens, are now saved by using by-product ovens?

4. Complete the following table relating to fuel gases:

NAME	CONSTITUENT GASES	RELATIVE HEAT VALUE	SOURCE
Coal gas			
Water gas			
Natural gas			
Producer gas			

5. How is the heat value of fuels expressed?

6. How can smoke be prevented?

7. Name the vapor and the gas that react together to produce the flame of a candle.

8. Make a diagram showing the three distinct parts, or regions, of a candle flame.

9. Which of the following statements is correct? The mixing of air with a fuel gas, as in the Bunsen burner, makes the flame hotter because (*a*) the flame is luminous; (*b*) the flame is nonluminous; (*c*) the combustion is complete.

10. Coal gas or acetylene issuing from a round pipe, when ignited, will burn with a luminous, smoky flame. (*a*) What makes the flame luminous? (*b*) Of what is the smoke composed? (*c*) How could you prevent the formation of smoke?

11. Write the equation for the reaction that takes place in the manufacture of water gas.

12. What name do we apply to (*a*) the tip of a candle flame? (*b*) the tip of the luminous cone of the flame?

13. (*a*) Name the reaction that occurs and the product formed when a metal is heated in that part of the flame designated by

(*a*) in question 12. (*b*) Also name the change that occurs and the product formed when a metal oxide, such as lead oxide, is heated in that part of the flame designated by (*b*) in question 12.

14. To what is the force of an explosion due?

15. Name two causes of mine explosions.

16. Explain how a flame can be so protected that it will not ignite an explosive mixture of air and combustible gas when submerged in it. What name is given to the lamp so constructed?

17. Name and describe the different kinds of electric furnaces.

THOUGHT QUESTIONS

1. (*a*) Why do we use a "choke" in starting an automobile? (*b*) Why do we use this device more in winter than in summer?

2. Why will not an automobile run if the choke is left on?

3. We learned in Chapter VII that 2 volumes of hydrogen combine with 1 volume of oxygen to form but 2 volumes of steam. Why, then, is a mixture of hydrogen and oxygen so explosive?

4. How do you account for the presence of nitrogen in (*a*) coal gas? (*b*) water gas? (*c*) producer gas?

5. (*a*) Why do the windows of rooms heated by portable gas stoves "sweat" in cold weather? (*b*) Is the moisture on the inside or the outside of the glass?

6. Suppose that in the manufacture of water gas you used 1000 lb. of coke containing 90 per cent free carbon. (*a*) What weight of steam would be decomposed by this amount of carbon? (*b*) Determine by inspection of the equation for the reaction the relative volumes of the gaseous products formed.

FOR HONOR STUDENTS

1. Read Chapter IX (entitled "Industrial Gases") in Volume I of "Chemistry in Industry," and report items of interest to the class.

2. Write to the Bureau of Mines, Washington, D. C., for papers on mine explosions, and report items of interest to the class.

CHAPTER XXXIV

ORGANIC COMPOUNDS — COMPOUNDS OF CARBON

480. ***Introduction.*** We have already studied a few of the compounds of carbon, including the oxides and the hydrocarbons. We shall now extend our study to other important compounds of this remarkable element. The compounds of carbon are often called *organic compounds,* since they make up a large part of all living things. There are probably 500,000 of them and the study of them is a separate branch of chemistry. We shall limit our study to a few of those compounds of importance in our everyday life.

I. The Carbohydrates

481. Definition. The name *carbohydrate* is applied to a group of compounds that includes the sugars, the starches, and cellulose. All these contain carbon, hydrogen, and oxygen, the last two elements nearly always being present in the proportion in which they combine to form water; hence the name *carbohydrate.*

482. Sucrose (cane sugar, beet sugar) ($C_{12}H_{22}O_{11}$). A great many different sugars are known, but *sucrose* is the one we buy at the grocer's and use for sweetening our foods. It is found in many plants, but the world's main supply comes from sugar cane and sugar beets (Fig. 214). Sugar cane grows only in warm climates (Cuba is the chief producer), while sugar beets thrive in cooler climates such as prevail in Colorado and Nebraska. We speak of *cane sugar* and *beet sugar* simply to indicate the source of the product; from either source it is the same compound, namely, sucrose.

483. Separation and refining of sucrose. The juice extracted from sugar cane or sugar beets contains the sucrose along with impurities. These impurities are removed by appropriate methods, and the resulting solution is then evaporated until the sucrose crystallizes out. The evaporation is carried out in large covered pans from which the air is partially removed (Fig. 216) to lower the boiling point of the solution so as to prevent the charring of the sucrose. The crystals are separated from the liquids by whirling the mixture at high speed in perforated vessels called *centrifugals* (Fig. 215). The saturated solution which remains when sugar cane is used as the source of the sugar is *molasses*. The impurities in beet-sugar juice have an unpleasant taste, so beet sugar must be highly refined. *Maple sugar* also consists of sucrose, its distinctive flavor being due to other substances present in the maple sap. The annual consumption of sucrose in the United States amounts to more than one hundred pounds for each inhabitant.

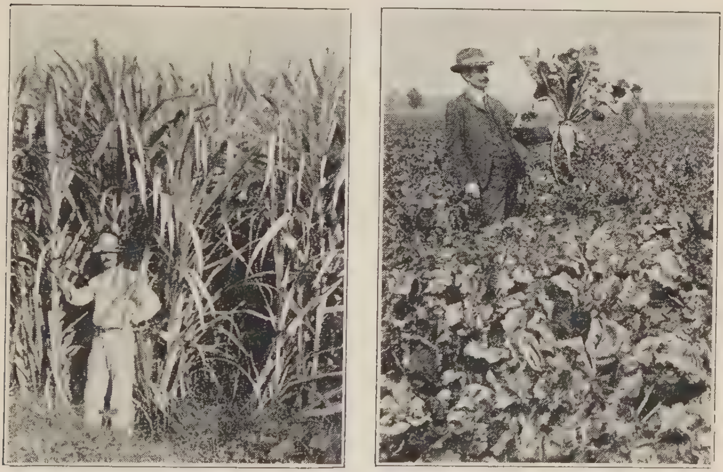


FIG. 214. Source of the world's output of sucrose, — the sugar cane and the sugar beet

484. Chemical conduct of sucrose. When a solution of sucrose is heated with hydrochloric acid (which acts as a catalyst) to about 70°, the sucrose and water react to form two simpler sugars, *dextrose* and *levulose,* each of which has the formula $C_6H_{12}O_6$.

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

In this reaction the sucrose is said to undergo *inversion,* and the mixture of equal parts of dextrose and levulose formed is called *invert sugar.*

When sucrose is heated to about 215°, a partial decomposition takes place and a brown substance is formed called *caramel.* This is used as a coloring matter in making confectionery.

485. Isomeric compounds. The thoughtful student will have noticed that dextrose and levulose, two entirely different compounds, have the same formula, namely, $C_6H_{12}O_6$, and will wonder how to account for this fact. The explanation is that the properties of a compound depend not only on the elements present, but even more on how the atoms of the elements are arranged in the molecule. While the molecules of dextrose and levulose are each made up of the same number of atoms of carbon, hydrogen, and oxygen, these atoms are arranged in one way in the molecule of dextrose and in a different way in the molecule of levulose — just as the checkers on a checkerboard may be arranged in two (or more) different ways. *Compounds that have the same formula are said to be isomeric compounds,* and there are many examples of these.

486. Lactose (milk sugar) ($C_{12}H_{22}O_{11}$). This sugar is not so sweet or soluble as sucrose, with which it is isomeric. It is a white solid, and is present in the milk of all mammals. The average composition of cow's milk is as follows:

Water	87.17%
Casein (nitrogen compounds)	3.56%
Butter fat	3.64%
Lactose	4.88%
Mineral matter	0.75%

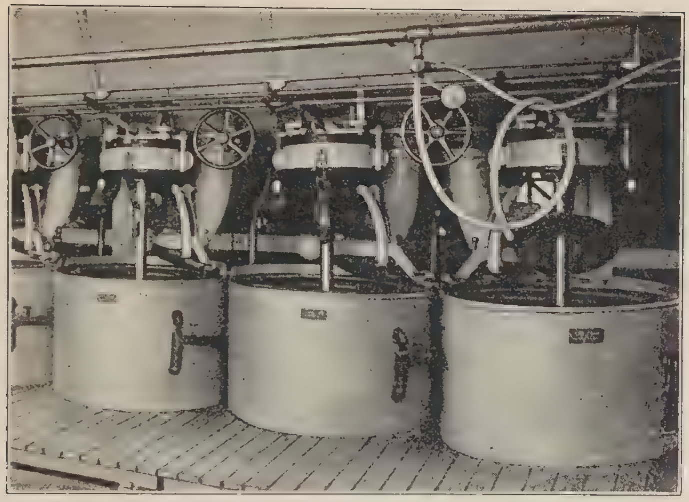


FIG. 215. Centrifugals for separating the sugar from sirup

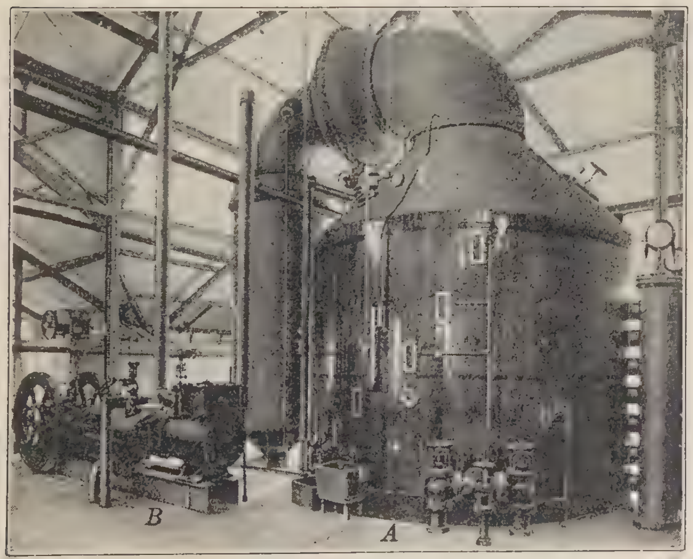


FIG. 216. Vacuum pans in a sugar factory

The air is pumped from the large covered pans *A* by the engine *B* the cheese its distinctive flavor. The formation of these compounds is caused by microörganisms which are added to the casein. Different organisms produce different flavors and hence different kinds of cheese.

488. Dextrose (grape sugar) ($C_6H_{12}O_6$). This sugar, whose formation from sucrose has been described (§ 484), occurs in honey and many fruits, usually associated with levulose. It is often called *grape sugar*, because of its presence in grape juice. It is prepared on a large scale by heating starch ($C_6H_{10}O_5$) with water containing a small percentage of hydrochloric acid, which acts as a catalyst:

$$C_6H_{10}O_5 + H_2O \longrightarrow C_6H_{12}O_6$$

If this action is carried to completion, pure dextrose is obtained. If it is not carried to completion, a thick sirup of dextrose mixed with other sugars results. This sirup is known as *glucose* or *corn sirup*. It is prepared in enormous quantities by heating the starch, water, and acid together in large copper retorts (Fig. 218). When the operation is complete, the acid present is neutralized with sodium bicarbonate (baking soda). Glucose is much cheaper than sucrose, although not so sweet. It is used in making candy, jellies, jams, and table sirups.

FIG. 220. When rennet is added to milk the casein separates (or sets) in the form of a porous solid

489. Starch ($C_6H_{10}O_5$). This compound is one of the most abundant of all the carbohydrates found in nature. It is formed only in the green parts of plants, in the presence of sunlight, by the direct union of carbon dioxide and water.

While the reaction is very complex, we may represent it in a simple way as follows:

$$6\ CO_2 + 5\ H_2O \longrightarrow C_6H_{10}O_5 + 6\ O_2$$

In the United States it is obtained chiefly from corn, about 60 per cent of which is starch. In Europe the potato serves as the principal source. It is prepared by grinding the corn or potato and then separating the various constituents present by taking advantage of their different densities, as explained in Fig. 221.

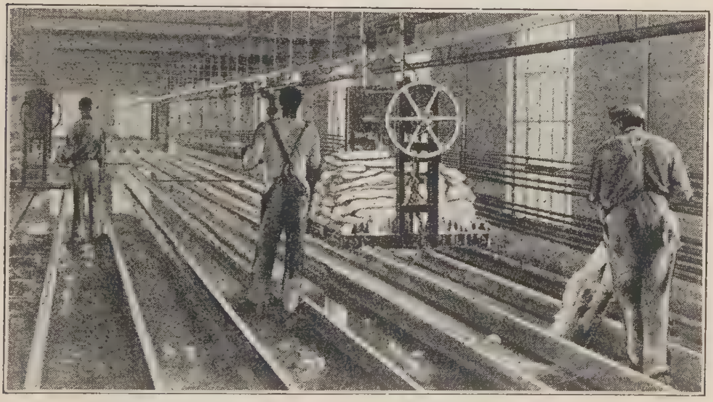


FIG. 221. Settling troughs in a starch factory

The ground corn (or potato) suspended in water flows slowly through long troughs. The starch settles to the bottom, while lighter materials, such as the seed germ, hulls, and pulp, float off at the end. After draining the troughs, the starch is removed with shovels

Starch consists of minute granules which differ somewhat in appearance according to their source (Fig. 222), so that it is generally possible to tell the source of any given sample by examining it under the microscope. When heated with water, these granules burst and the starch partially dissolves; hence starchy foods become more digestible by cooking. When roasted under proper conditions, starch is converted into a soluble carbohydrate known as *dextrin*. It is used in making pastes and mucilage, such as we find on the back of postage stamps.

490. Cellulose ($C_6H_{10}O_5$). All vegetable structures contain a large percentage of cellulose. When wood fibers are treated with various reagents, especially sodium sulfite, the other substances present are dissolved, leaving the pure cellulose. The filter paper used in the laboratories has been treated in this way; so has absorbent cotton. Cotton and linen are likewise principally cellulose.

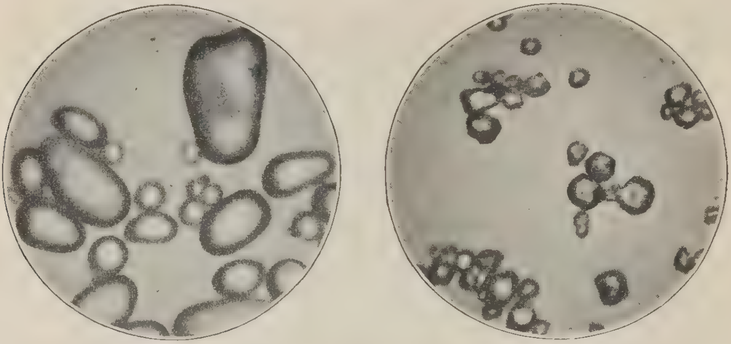


FIG. 222. Granules of wheat starch (at left) and of corn starch (at right) (magnified 290 times)

Cellulose is insoluble in all ordinary reagents, but will dissolve in certain mixtures, such as a mixture of sodium hydroxide and carbon disulfide. It is insoluble in sodium hydroxide, but water in the presence of concentrated hydrochloric acid changes it into dextrose:

$$C_6H_{10}O_5 + H_2O \longrightarrow C_6H_{12}O_6$$

Ripened stalks of any plant consist mainly of cellulose, and experiments are being made to find a practical method for converting the cellulose of cornstalks into paper, boards, and other useful products, so as to utilize the enormous quantities of cornstalks that now go to waste. These ex-

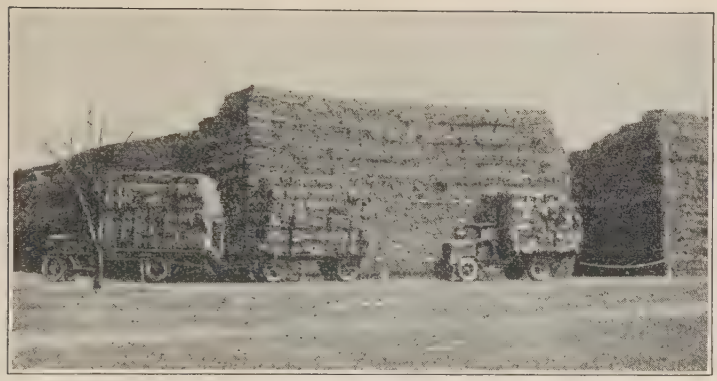


FIG. 223. Stacks of cornstalks at a factory

It is estimated that the United States produces 150,000,000 tons of cornstalks annually. This material is largely cellulose and from it can be made paper and various grades of wall board and substitutes for rough lumber. Interesting products are also obtainable from the distillation of corncobs that may find uses in the industries. Companies have been formed and plants erected to test the economic values of all these materials. If successful, these processes will change what is now a nuisance to the farmer into a source of profit

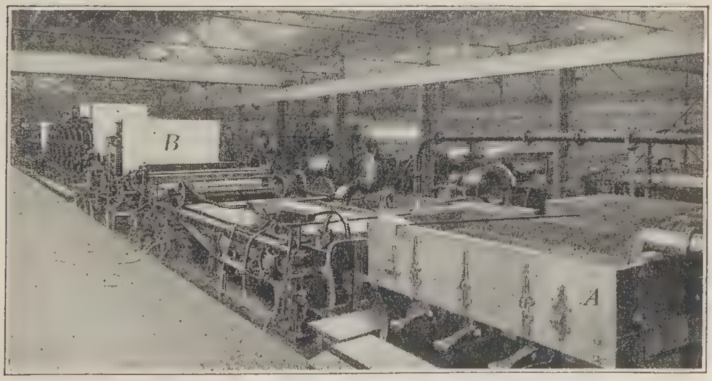


FIG. 224. View of the interior of a paper mill

The tank *A* contains the paper pulp and other materials, mixed with water. The mixture is run onto metal screens, through which the water runs. The pulp is then passed between large metal cylinders, some of which are heated with steam. The pulp is thus pressed into the form of paper, *B*, and wound into large rolls

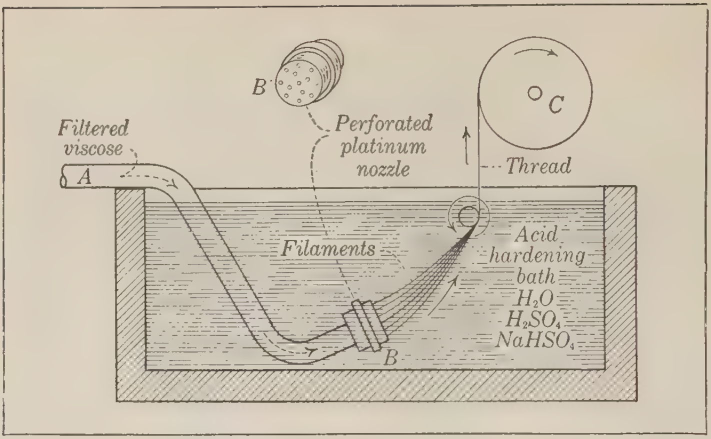

B′
Filtered viscose
A
Perforated platinum nozzle
C
Thread
Filaments
Acid hardening bath
H_2O
H_2SO_4
$NaHSO_4$
B

FIG. 225. Making rayon threads

Pure cellulose, dissolved in a suitable solvent (viscose, *A*), is forced through small holes in the plate *B* (*B′*), and emerges into the hardening bath in the form of fine threads. These are twisted into a coarser thread and wound up on the reel *C*

FIG. 226. View in a plant for making rayon

Sorting rayon threads according to size and quality periments are proving successful, and large factories have been built for converting the cornstalks into commercial products (Fig. 223).

491. Paper. Paper consists mainly of cellulose. Certain other materials are added in the course of its manufacture, such as finely ground calcium sulfate, to give body to the paper. The finer grades of paper are made from cotton and linen rags, and the cheaper grades from wood.

In making paper from wood, the trees (mostly spruce and hemlock) are cut into fine chips and the chips heated with sodium hydroxide or calcium acid sulfite, which removes the objectionable matter from the cellulose. This is then bleached with chlorine. In this way the cellulose is obtained in the form of thin white shreds suspended in water, known as *paper pulp.* Certain other materials, varying with the kind of paper desired, are next mixed with the pulp. Thus, calcium sulfate or clay is added to give "body" to the paper. The mixture is then run onto screens, dried and pressed into the form of paper, as shown in Fig. 224.

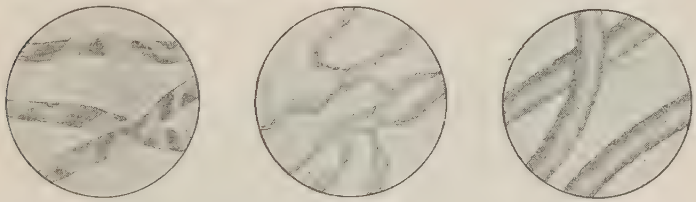

Silk fiber Cotton fiber Wool fiber

FIG. 227. Textile fibers (highly magnified)

492. Characteristics of various textile fibers. Of the different fibers used in making the yarns from which the common fabrics are made, the vegetable fibers, cotton and linen, are essentially cellulose, while the animal fibers, wool and silk, are composed of nitrogenous substances. To the naked eye these fibers look much alike, but when examined with the microscope their appearance varies widely (Fig. 227).

It is also possible to distinguish between the fibers by the action of chemical reagents. For example, a hot solution of sodium hydroxide (5 per cent to 10 per cent) has but little action upon cotton, while it will readily dissolve wool and slowly dissolve silk. The nitrogenous fibers burn with an unpleasant odor like that of burning hair, and this property is sometimes useful in determining the source of a fiber.

493. Rayon; cellophane; mercerized cotton. Silk has long been known and highly prized; it is mentioned in the Bible. The silk fiber is spun by silkworms, which are grown in large numbers for this purpose, especially in Japan and China. Because of the high cost of silk an effort has long been made to produce a cheaper product that will have the appearance and properties of the natural product. This has led to the production in large quantities of artificial silk, to which the name *rayon* has been given.

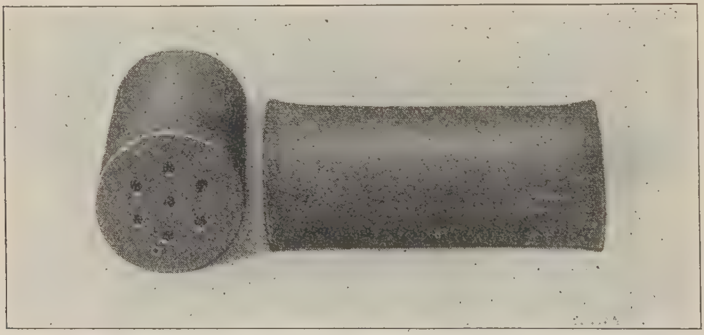


FIG. 228. Grains of smokeless powder for large guns (natural size)

Rayon is a form of cellulose, while the natural silk is a mixture of compounds of nitrogen, so that although they look alike, it is easy to distinguish between the two (§ 492). The most common method of making rayon is shown in Figs. 225, 226. The United States leads in the production of rayon, making about 130,000,000 lb. annually. The wrapping material known as *cellophane* has the same composition as rayon and is made in the same way, except that it is produced in the form of transparent sheets rather than threads.

Another form of cellulose that has a silklike appearance is known as *mercerized cotton.* This is made by treating cellulose with a cold concentrated solution of sodium hydroxide.

494. Cellulose nitrates (nitrocellulose). Nitric acid (mixed with sulfuric acid) acts on cellulose much as it does on bases, forming a mixture of *cellulose nitrates,* commonly known as *nitrocellulose.* These are white solids, but they can also be obtained in transparent form. Nitrocellulose is very inflammable, and under certain conditions highly explosive.

Nitrocellulose is a very important substance, as is shown by the following uses: (1) it is the chief constituent of *smokeless powders* for guns (Fig. 228); (2) *photographic films* are made from the transparent form, also from a similar compound known as *cellulose acetate* (Fig. 229); (3) it is the basis of the *lacquers* now so widely used under many trade names, especially for painting automobiles; (4) it is an important constituent of many varieties of *artificial leather*; (5) *collodion,* which we buy from the druggist and use in place of court plaster, consists of a solution of nitrocellulose in a mixture of alcohol and

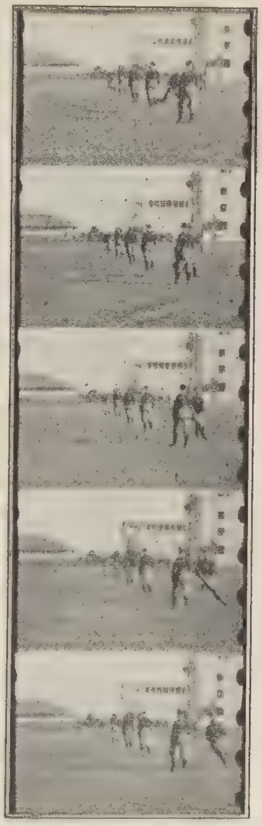


FIG. 229. A section of a movie film made of cellulose acetate

ether; (6) *celluloid* is a mixture of nitrocellulose and camphor (a white solid obtained from the camphor tree grown in Japan), often colored by various dyes. *It should be kept in mind that nitrocellulose is highly inflammable and therefore that substances made from it are likely to burn readily.* Many serious accidents have resulted from the careless use of these substances.

SUMMARY OF PART I OF CHAPTER, IN QUESTION FORM

1. What are the compounds of carbon often called?

2. One of the most important groups of organic compounds is the *carbohydrates.* What does the name indicate concerning (*a*) the elements present in the compounds belonging to this group? (*b*) the relative numbers of atoms of two of the elements present?

3. Distinguish between carbohydrates and hydrocarbons.

4. Complete the following table relating to the important sugars:

CHEMICAL NAME	COMMON NAME	CHIEF SOURCE	USES
1.			
2.			
3.			
4.			

5. (*a*) Write the equation for the reaction that takes place when sucrose is heated with water and hydrochloric acid. (*b*) Give the name of each of the compounds formed; (*c*) also the name given to the mixture of these compounds.

6. What name is given to a coloring matter made from sucrose, that is used in making confectionery?

7. The formula $C_6H_{12}O_6$ may represent either dextrose or levulose — two entirely different sugars. (*a*) What name do we apply to compounds that have the same formula? (*b*) How do we account for the fact that two (or more) different compounds may have the same formula?

8. To what is due (*a*) the sweet taste of fresh milk? (*b*) the sour taste of milk that has stood for some time?

9. (*a*) What causes the souring of milk? (*b*) How can it be delayed? (*c*) Why does the milk curdle?

10. Tell what is formed in each of the following cases:
(*a*) Starch + boiling water
(*b*) Starch + dilute hydrochloric acid
(*c*) Sweet milk + rennet
(*d*) Starch + heat (roasting)
(*e*) Cellulose + concentrated hydrochloric acid
(*f*) Cellulose + nitric acid (mixed with sulfuric acid)

11. State which of the following words are closely associated with the separation and refining of sugar: caramel, centrifugals, isomeric, fermentation, vacuum, pasteurization, molasses, levulose.

12. Name three substances that are pure, or nearly pure, cellulose.

13. The solubility of cellulose in a mixture of sodium hydroxide and carbon disulfide finds a practical application in the manufacture of what textile?

14. Give the common name of the substance, either white or transparent, that is an important constituent of smokeless powder, photographic films, lacquers, artificial leather, collodion, and celluloid.

15. What treatment would you give a piece of cloth to determine whether it is cotton, natural silk, rayon, or wool?

FOR HONOR STUDENTS

Read one of the following chapters and write a theme on the subject, reporting items of special interest to the class: Chapter IX (entitled "The Rival Sugars") in "Creative Chemistry"; Chapter VII (entitled "Sugar and Sugar Crops") in "Chemistry in Agriculture"; Chapter X (entitled "What comes from Corn") in "Creative Chemistry."

II. The Alkaloids

495. General discussion. We have seen in this chapter that plants furnish us with food and clothing. They also furnish us with many useful medicines. Prominent among these is the class of substances known as *alkaloids* because they have the properties of bases. Each of these is found in some part of a certain plant. Thus, *caffeine* is always present in the coffee berry and tea leaves and is their active constituent. Some of the most important alkaloids are *quinine, morphine, strychnine,* and *cocaine.* All of these are solid white compounds containing carbon, hydrogen, oxygen, and nitrogen. *Nicotine,* the active constituent of tobacco, is one of the few liquid alkaloids.

The alkaloids, as a rule, are very active, and most of them are intensely poisonous. Some of them, such as cocaine and morphine, are very dangerous habit-forming drugs.

III. The Alcohols.

496. General discussion. Just as there are a great many sugars, so there are a great many alcohols, each containing the OH radical. The two most important ones are *methanol* (CH_3OH) and *ethyl alcohol* (C_2H_5OH). The latter compound is ordinary alcohol. Both of these alcohols are colorless, inflammable liquids. Methanol may be regarded as derived from methane (CH_4), and ethyl alcohol from ethane (C_2H_6), by substituting an OH group for an atom of hydrogen.

497. Methanol (methyl alcohol, wood alcohol) (CH_3OH). This alcohol is called *methanol* in order to distinguish it from ordinary alcohol. It is formed when hard woods, such as beech, are heated in the absence of air, and on this account is often called *wood alcohol.* Increasing amounts are now being made by heating carbon monoxide and hydrogen under suitable conditions:

$$CO + 2\,H_2 \longrightarrow CH_3OH$$

It boils at 64.5°, and burns with an almost colorless flame. It is a good solvent for organic substances, and is widely used for this purpose. It is highly poisonous, and many deaths have occurred from its use in beverages as a fraudulent substitute or adulterant for ordinary alcohol. It also acts upon the optic nerve, and many persons have become blind from drinking the liquid or inhaling its vapor.

When a mixture of the vapor of methanol and air is passed over hot copper (a catalyst), a gaseous compound known as *formaldehyde* (CH_2O) is formed:

$$2\,CH_3OH + O_2 \longrightarrow 2\,CH_2O + 2\,H_2O$$

A 40 per cent solution of this gas in water is sold under the name of *formalin*. Large quantities of this are used as a disinfectant and preservative.

498. Ethyl alcohol (grain alcohol, alcohol) (C_2H_5OH). This compound is the one commonly known as alcohol. It is a colorless liquid with a pleasant odor, and is an excellent solvent for many organic substances. It boils at 78.5°. It is sometimes used as a fuel, since its flame is very hot and does not deposit carbon as the flame from oil does. When taken into the system in small quantities it causes intoxication; in larger quantities it acts as a poison. The intoxicating properties of such liquors as wine and whisky are due to the alcohol in them. The ordinary alcohol of the druggist contains about 95 per cent of alcohol and 5 per cent of water. A solution containing 99 per cent or more of alcohol is called *absolute alcohol*. When alcohol is heated with sulfuric acid, a low-boiling, inflammable liquid known as *ether* is formed:

$$2\,C_2H_5OH \longrightarrow (C_2H_5)_2O + H_2O$$

This is largely used as an anæsthetic in surgical operations.

499. Preparation of ethyl alcohol. Alcohol is prepared by the action of ordinary baker's yeast upon different sugars, such as dextrose:

$$C_6H_{12}O_6 \longrightarrow 2\,C_2H_5OH + 2\,CO_2$$

This process, in which a sugar is changed into alcohol and carbon dioxide by the action of yeast, is known as *alcoholic fermentation.* The yeast is a low form of plant life (Fig. 230), and thrives in appropriate sugar solutions. As it grows it secretes a substance known as *zymase,* and it is the zymase that acts upon the sugar, changing it into alcohol and carbon dioxide.

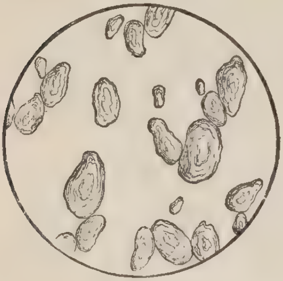


FIG. 230. Some cells of the yeast plant (magnified)

Most of the alcohol used in the United States for commercial purposes is made by the fermentation of the sucrose present in crude molasses. A limited amount is made from starch. In the latter case the starch is first mixed with malt (Fig. 231). This consists of barley which has been kept in a moist, warm place until the grains sprouted and has then been heated until the germ is killed. As the grain sprouts there is produced a small percentage of a substance known as *diastase,* which acts on the starch, changing it into a sugar known as *maltose.* Yeast acts on the maltose just as it does on dextrose, changing it into alcohol and carbon dioxide. The alcohol is separated by fractional distillation.

FIG. 231. Malt for preparing maltose

500. The alcohol problem. From very ancient times men of all nations have prepared alcoholic liquors of various kinds as beverages. In alcoholic content these range from 3 to 5 per cent in beers and light wines to 50 per cent and higher in distilled whisky and brandy. Governments have found these beverages to be a fruitful source of revenue and have imposed heavy taxes on all kinds of fermented and distilled liquors, carefully supervising their manufacture. They have also taxed pure alcohol heavily because imitation beverages can be made very easily from pure alcohol. In the United States the tax on 95 per cent alcohol is $2.10 per gallon. Even with this tax, the sale of alcohol is limited to a very few definite uses, chiefly medicinal in character.

On the other hand, alcohol has important scientific and industrial uses for which no good substitute can be found, and the government has no desire to interfere with these uses, which the Federal prohibition act defines very carefully. Accordingly, educational and scientific institutions can obtain alcohol for scientific uses, tax free, and for industrial purposes the government allows the use of *denatured* alcohol, which is also tax free. Denatured alcohol is alcohol to which has been added a definite amount of some substance which renders it unfit for use as a beverage but which does not impair its use for manufacturing. The substances which may be added for this purpose are prescribed by the Federal government and are known as *denaturants*. Among these are methanol and benzine.

501. Ethylene glycol ($C_2H_4(OH)_2$). If we replace one atom of hydrogen in ethane (C_2H_6) by an OH group, ethyl alcohol (C_2H_5OH) results. If we replace two atoms of hydrogen by two OH groups, there is formed the compound $C_2H_4(OH)_2$, known as *ethylene glycol.* This compound, a colorless sirupy liquid, is used in automobile radiators in winter time because it does not readily freeze.

502. Enzymes. Attention has been called to the action of *zymase* (§ 499) and of *diastase* (§ 499). These belong to a class of substances known as enzymes. *An enzyme is a substance secreted by a living organism which acts as a catalyst in certain chemical changes.* Our bodies contain a number of these; for example, *ptyalin* in the saliva, which changes the starch of our foods into a soluble sugar — the first step in the process of digestion.

503. Chemical changes in bread-making. The average composition of wheat flour is as follows:

Water	11.9%
Gluten (nitrogenous matter)	13.3%
Fats	1.5%
Starch	72.7%
Mineral matter	0.6%

In making bread, flour is mixed with water, yeast, and a little sugar, and the resulting dough is set aside in a warm place for a few hours. The yeast first causes the sugar to undergo alcoholic fermentation. The carbon dioxide formed escapes through the dough, making it light and porous. The yeast plant thrives best at about 30°; hence the necessity for keeping the dough in a warm place. In the process of baking the heat expels the alcohol and also expands the bubbles of carbon dioxide caught in the dough, causing the dough to become porous and making the bread light.

504. How foods may be kept from spoiling. We have seen that such changes as the souring of milk and the fermentation of sugar are due to the presence of minute organisms. Many other changes, such as *putrefaction*, are due to the same cause. Since the spores of these organisms are present in the air, they easily find their way into the foods and start the changes, so that it is difficult to keep foods from spoiling. Some of the ways for doing this are the following: (1) The food may be kept in a cold place, and the growth of the organism delayed by the low temperature. (2) The food may be heated until all the organisms present are destroyed, and then sealed in air-tight containers. Canned vegetables are kept sweet in this way. Any substance treated so as to destroy all organisms present is said to be *sterilized* (Fig. 232). (3) We may dry the food so that the organisms have not enough moisture to grow. (4) We may add so much of some food material, such as salt or sugar, that the medium is too concentrated for the organism to grow in. (5) Finally, we may add some compound, a small percentage of which will prevent the growth of the organisms; such is the acetic acid (§ 506) contained in vinegar, or the smoke which enters into a smoked ham. Such a substance is known as a *preservative*. Of course we must be on our guard against using as a preservative in food any substance injurious to human health. United States law forbids the use of many preservatives in food destined for general commerce; it allows *sodium benzoate* only under certain restrictions, one of which is that the label must state the percentage used. In preserving a food, cleanliness and sterilization are better than an added preservative.

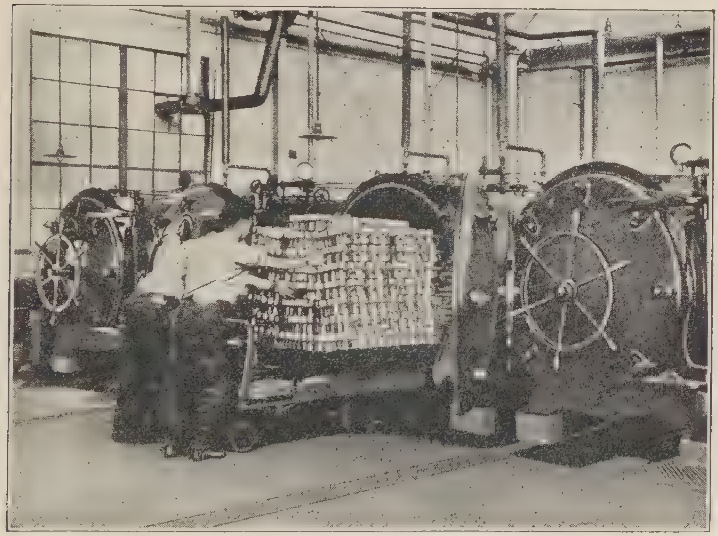


FIG. 232. Sterilizing canned vegetables

The prepared vegetables are placed in cans, run into large boilers, and heated until all organisms present are destroyed; the cans are then sealed air-tight

SUMMARY OF PARTS II AND III OF CHAPTER, IN QUESTION FORM

1. (*a*) What name is applied to a group of basic compounds found in plants? (*b*) Mention one use of many of these compounds.

2. What radical is common to all alcohols?

3. Complete the following table relative to the two most common alcohols:

CHEMICAL NAME	COMMON NAME	CHIEF COMMERCIAL SOURCE	USE
1. 2.			

4. Complete the equation and name the product represented by the formula not printed:

$$2\ CH_3OH + O_2 \longrightarrow 2\ H_2O + \text{------}$$

5. (*a*) Give the name applied to the change which takes place when yeast is added to a solution of dextrose. (*b*) Name the products formed in this change.

6. For what purposes are such substances as methanol and benzine added to ethyl alcohol?

7. What name is given to the catalysts secreted by certain living organisms?

8. (*a*) What compounds are produced through the action of yeast in bread-making? (*b*) Do these compounds remain in the finished bread?

9. Write the equation for the reaction that takes place when (*a*) ethyl alcohol is burned; (*b*) when methanol is burned.

10. Supply the missing words: When barley grain sprouts, there is produced an ------ known as ------. This has the property of changing ------ into a sugar known as ------. Yeast acts on this sugar, changing it into ------ and ------.

11. Give two reasons for taxing alcohol.

12. (*a*) What causes food to spoil? (*b*) Mention three ways of preventing foods from spoiling.

13. State which of the following words would be used in describing the manufacture of alcohol from molasses: malt, carbon dioxide, pyridine, starch, enzyme, yeast, maltose, fractional distillation, zymase, diastase.

FOR HONOR STUDENTS

Read Chapter III (entitled "Alcohol and Some Other Solvents") in Volume I of "Chemistry in Industry," and report points of interest to the class.

IV. Organic Acids and their Derivatives

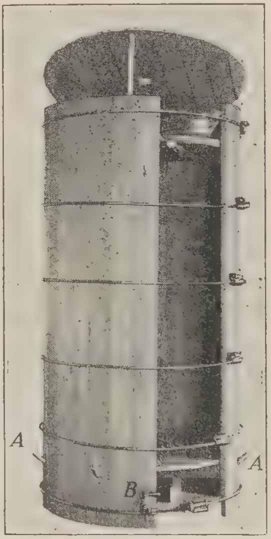
505. General discussion. The sour taste of certain foods tells us of the presence of acids. Thus, *acetic acid* is present in vinegar, *citric acid* in lemons and grape fruit, and *lactic acid* in sour milk. These acids are known collectively as the *organic acids*. They occur either in the form of the free acid or as some derivative of the acid. We shall now study a few of the most important of these.

506. Acetic acid ($C_2H_4O_2$, generally written as $H \cdot C_2H_3O_2$). This is the acid which imparts the sour taste to vinegars. While each molecule contains four atoms of hydrogen, only one of these can be replaced by a metal to form a salt. Acetic acid is therefore a monobasic acid (§ 350), and we indicate this fact in the formula by separating the replaceable hydrogen atom from the rest of the molecule, thus: $H \cdot C_2H_3O_2$.

Acetic acid is prepared on a large scale by the destructive distillation of wood (§ 159, 2). It is a colorless liquid and has a strong, pungent odor. Many of the salts of acetic acid (*acetates*) are well-known compounds. Thus, lead acetate ($Pb(C_2H_3O_2)_2 \cdot 3\ H_2O$) is the white solid known as *sugar of lead*.

507. Vinegar. As is well known, when cider is exposed to the air it is gradually transformed into vinegar. Two changes are involved in the process: (1) the sugar in the cider first undergoes alcoholic fermentation, forming *hard cider*, which contains from 4 to 8 per cent of alcohol; (2) the alcohol is then oxidized to acetic acid, the necessary oxygen coming from the air. This oxidation is brought about through the action of a minute organism. The oxidation of alcohol into acetic acid through the agency of the organism is known as *acetic fermentation*, and may be represented as follows:

$$C_2H_5OH + O_2 \longrightarrow H \cdot C_2H_3O_2 + H_2O$$



The generator is filled loosely with beech shavings. Vinegar is first sprayed into the top of the cask in order to introduce the essential organism. This organism attaches itself to the shavings, which are used because they present a large surface. Next, a dilute solution of alcohol (hard cider, in the case of cider vinegar) is sprayed into the top of the cask while air is admitted at the bottom *A*, *A*. In this way the alcohol and oxygen are brought into intimate contact, and the oxidation takes place rapidly as the liquid trickles down over the shavings. The resulting vinegar is drawn off at the bottom *B* of the cask

FIG. 233. A generator for the manufacture of vinegar

508. Manufacture of vinegar. The old method of making vinegar consisted simply in storing cider in barrels until the fermentation was complete — a process requiring several weeks. In the modern method the change is brought about in a few hours, a large cask known as a *generator* being used (Fig. 233). Instead of starting with cider, one may use almost any substance which contains starch or sugar, these compounds first being changed into alcohol, as explained in the manufacture of alcohol. In this way we prepare *malt vinegar* from starch and *sugar vinegar* from sugar residues. The cheapest vinegar is made from ordinary dilute alcohol and is known as *distilled vinegar*. It is colorless and leaves no residue upon evaporation.

The Federal law requires that all vinegar shall contain not less than 4 per cent of acetic acid. In addition to the acid, vinegar prepared from fruits and grains contains certain solids derived from the source materials. It is by studying the character of these solids left upon evaporating a sample of vinegar that the chemist is able to determine the source of the vinegar.

FIG. 234. Argols, the source material of cream of tartar

509. Tartaric acid ($H_2 \cdot C_4H_4O_6$). This is a white crystalline solid, and occurs in many fruits either in the free state or in the form of its salts. It is dibasic, as is indicated in its formula. The acid potassium salt ($KH \cdot C_4H_4O_6$) occurs in the juice of grapes. When the juice ferments in the manufacture of wine, this salt, being insoluble in alcohol, separates on the sides of the cask; in this form it is known as *argol* (Fig. 234). When purified it forms a white solid, which is sold under the name of *cream of tartar* and is used in baking powders. The acid itself is often used in soft drinks.

510. Palmitic acid, stearic acid, oleic acid. These three acids, closely related to each other, are of the greatest importance to us, since their derivatives are the chief constituents of many fats and oils, such as butter and olive oil, which we use as foods. They are all monobasic acids, as the following formulas show:

Palmitic acid ($H \cdot C_{16}H_{31}O_2$)	a white solid melting at 64°
Stearic acid ($H \cdot C_{18}H_{35}O_2$)	a white solid melting at 69°
Oleic acid ($H \cdot C_{18}H_{33}O_2$)	a colorless oily liquid

511. Oils and fats derived from animal and vegetable sources. In addition to the hydrocarbon oils derived from petroleum, there is another large class of oils and fats derived from animal and vegetable sources. Almost every seed and fruit, as well as the tissues of animals, contains one or more oils which can be squeezed out by pressure. Thus we have olive oil, palm oil, corn oil, coconut oil, cod-liver oil, cottonseed oil, and a host of others. These oils are entirely different in composition and chemical conduct from the petroleum oils, being composed of derivatives of certain acids.

STEARIN
PALMITIN
OLEIN

FIG. 235. The three chief constituents of oils and fats

Just as each molecule of an acid contains one or more hydrogen atoms that can be replaced by metals to form *salts*, so this same hydrogen can be replaced by hydrocarbon radicals, as CH_3 (methyl), C_3H_5 (glyceryl), to form compounds known as *esters*. *Now the chief constituents of the vegetable and animal oils and fats are glyceryl esters of palmitic, stearic, and oleic acids, and are known as palmitin, stearin, and olein* (Fig. 235). These are formed from the corresponding acids by displacing the hydrogen of the acid by the glyceryl radical C_3H_5. This radical has a valence of 3, and since each molecule of palmitic, stearic, and oleic acids is monobasic, it follows that three molecules of each of these acids must enter into the formation of one molecule of the ester derived from the acid. These relations are shown in the following formulas:

$H \cdot C_{16}H_{31}O_2$ (palmitic acid)	$C_3H_5(C_{16}H_{31}O_2)_3$ (palmitin)
$H \cdot C_{18}H_{35}O_2$ (stearic acid)	$C_3H_5(C_{18}H_{35}O_2)_3$ (stearin)
$H \cdot C_{18}H_{33}O_2$ (oleic acid)	$C_3H_5(C_{18}H_{33}O_2)_3$ (olein)

Palmitin and stearin are white solids, the chief constituents of the solid fats. Olein is a liquid and makes up a large part of the oils such as olive oil.

In separating oils from their source material, we are sure to obtain along with the oil some other substances dissolved in the oil. Sometimes these substances add to the flavor of the oil, as is the case with olive oil; more often they impair its looks and taste. Thus, the crude cottonseed oil (Fig. 236) and corn oil are black and not edible. It is possible to remove the impurities, and the oils when so refined are very much alike in composition. Thus, the refined corn oil and cottonseed oil (Fig. 236) are now largely used as salad oils in place of the more expensive olive oil, and only an expert can distinguish between them.

512. Butter fat and oleomargarine. While butter fat, like other fats, consists principally of palmitin, stearin, and olein, its characteristic flavor is due to the presence of small quantities of other fats present in milk. Oleomargarine differs from butter mainly in the fact that a smaller percentage of the fats characteristic of butter is present. It is made from the fats obtained from cattle and hogs. Sometimes vegetable oils, such as coconut oil and cottonseed oil, are used. These fats are churned with milk or mixed with a small quantity of butter, in order to furnish the necessary fat to give the flavor of butter.

While it is a common practice to color butter, the Federal laws permit the coloring of oleomargarine only upon the payment of a tax of 10 cents for each pound colored. Some of the states forbid the sale of colored oleomargarine even if the tax is paid.

513. Changing oils into solid fats: the hydrogenation of oils. It will be noted that stearin differs from olein in composition in that it contains six more atoms of hydrogen in each molecule (§ 511). Now when hydrogen is brought in contact with olein under the proper conditions and in the presence of a suitable catalyst (finely divided nickel is used), the olein takes up the additional hydrogen and is changed into solid stearin. It is possible in this way to change the oils into solid fats (Fig. 236). Certain commercial fats used in cooking, mostly sold under trade names, are made by this process from the comparatively inexpensive cottonseed oil and used in place of lard.

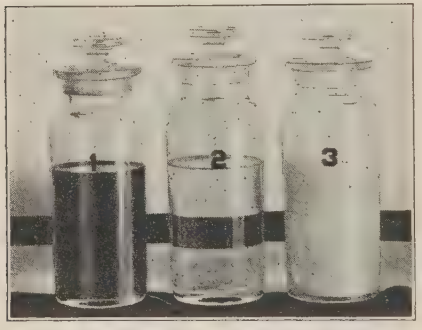


FIG. 236. Cottonseed oil

In jar 1 is the crude cottonseed oil as pressed from the seed, in jar 2 the refined oil, and in jar 3 the oil after hydrogenation

V. Soaps

514. Composition and manufacture of soaps. Someone has said, "Tell me the amount of soap used per thousand inhabitants of a nation, and I will tell you how far advanced in civilization that nation is." Whether or not this claim could be made good, it is certain that soap contributes much to the welfare of any people. A study of its composition and manufacture properly belongs with the study of fats and oils, since these are the main compounds used in its manufacture.

To prepare soap we have but to heat a fat (or oil) with a solution of sodium hydroxide. In the process the palmitin, stearin, and olein composing the fat are converted into glycerin (often called glycerol) and sodium palmitate, sodium stearate, and sodium oleate. *A mixture of these three salts constitutes soap.* The reactions may be illustrated by the following equation:

$$\underset{\text{stearin}}{C_3H_5(C_{18}H_{35}O_2)_3} + \underset{\text{sodium hydroxide}}{3\ NaOH} \longrightarrow \underset{\text{glycerin}}{C_3H_5(OH)_3} + \underset{\text{sodium stearate}}{3\ NaC_{18}H_{35}O_2}$$

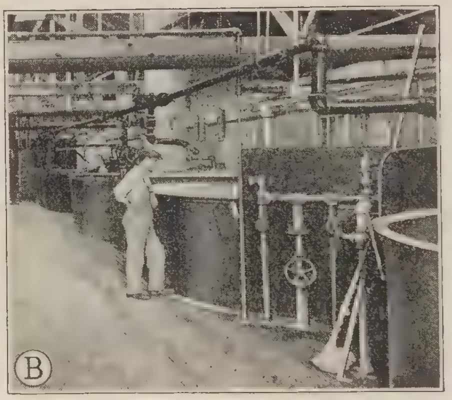
When the reaction between the fat and sodium hydroxide is complete, the soap and the water present form a colloidal dispersion. The soap is separated by the addition of salt, which causes the colloid to coagulate. This cannot be done with a potassium soap, which therefore remains an unpurified "soft soap." The remaining liquid contains the glycerin formed in making the soap. This is the source of all our glycerin, so that every soap factory is a glycerin factory as well. Some of the steps in the manufacture of soap are shown in Fig. 237.

515. Different kinds of soap. There are many different kinds of soap, their difference depending partly on the particular fat used and partly on the addition of certain other substances to the soap. Thus, *floating soaps* owe their lightness to bubbles of air. *Naphtha soaps* contain a small percentage of naphtha. *Scouring soaps* contain some finely powdered sand or volcanic ash. Sometimes sodium carbonate or borax is added to soap. Perfumes and coloring matter may also be present.

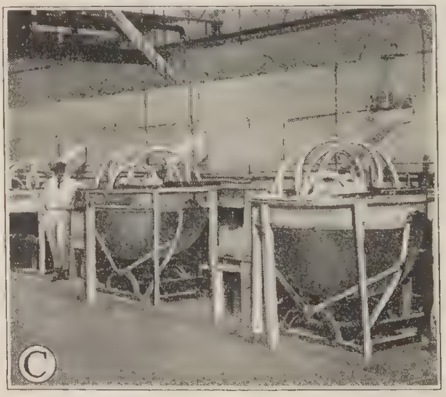
516. Properties of soap. When added to soft water, soap seems to dissolve; in reality the soap forms with the water a colloidal dispersion (§ 438) which is slightly alkaline in reaction. If an acid, such as hydrochloric acid, is added to

SODIUM HYDROXIDE
TALLOW
COTTON-SEED OIL
COCONUT OIL
PALM OIL
RESIN
A

The essential materials are (1) an animal or vegetable fat or oil and (2) an alkali. The fats and oils used are tallow and cheap vegetable oils, such as cottonseed oil, palm oil, and coconut oil. The alkali used is sodium hydroxide. Resin may be used instead of fat



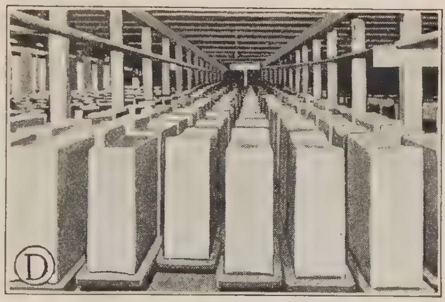
The melted fat or the oil is heated with a solution of sodium hydroxide in large iron kettles. These kettles are so large that 500,000 lb., or even more, of soap may be made at one time. The resulting soap forms a colloidal suspension in the water present and is separated by adding sodium chloride,— a process known as "salting out"



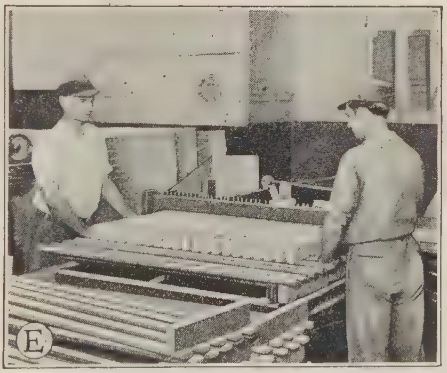
The soap when separated is stringy or fibrous. To overcome this and also to make it uniform, the soap is pumped into large stirring bowls, or "crutchers," and stirred until it is uniform. If it is desired to add other materials (§ 515),. they are added and mixed with the soap in the crutchers

FIG. 237, A, B, C. Some steps in the manufacture of soap

The soap while still fluid is allowed to flow from the stirring bowls into large boxes, or frames, open at the top. When the soap has hardened, the sides of the boxes are removed, leaving large cakes of soap as can be seen in D



The large cakes of soap shown in D are next cut by machinery first into flat slabs, then into long bars, and finally into cakes of appropriate size, depending upon their quality and use



As the final step in its manufacture the soap is stamped and wrapped by means of special machinery, and is now ready for the market

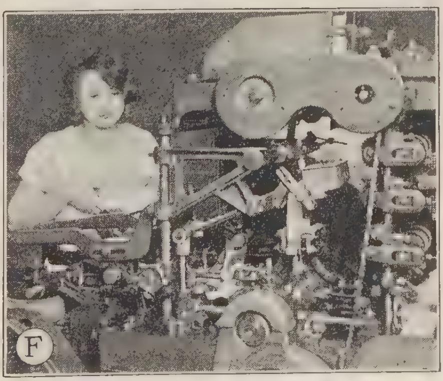


FIG. 237, D, E, F. Some steps in the manufacture of soap the colloidal dispersion, the organic acids are liberated from their salts and, being insoluble, are precipitated:

$$\underset{\text{sodium stearate}}{NaC_{18}H_{35}O_2} + HCl \longrightarrow NaCl + \underset{\text{stearic acid}}{H \cdot C_{18}H_{35}O_2}$$

The calcium and magnesium salts of oleic, palmitic, and stearic acids are insoluble in water and are therefore precipitated when a calcium or magnesium compound is added to a colloidal dispersion of soap (Fig. 238):

$$2\ \underset{\text{sodium stearate}}{NaC_{18}H_{35}O_2} + CaCl_2 \longrightarrow 2\ NaCl + \underset{\text{calcium stearate}}{Ca(C_{18}H_{35}O_2)_2}$$

It is due to this fact that soaps do not lather with hard waters but form a curdy precipitate, since such waters always contain calcium and magnesium salts in solution.

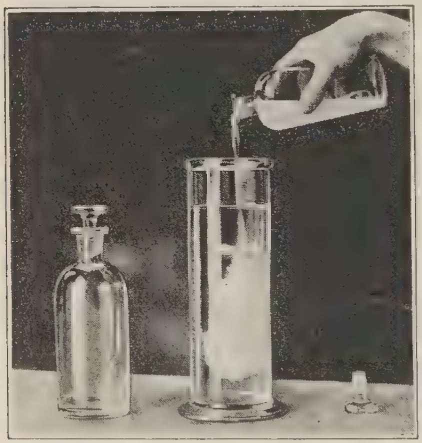


FIG. 238. When solutions of soap and a calcium salt are mixed, a white precipitate of calcium stearate forms

The cleansing action of soap is not thoroughly understood, but seems to be associated with the property which soap possesses of forming emulsions (§ 445). When soap is rubbed on the skin any oily substances present are emulsified and washed away. Adsorption also plays an important part. The dirt particles are more strongly adsorbed by the colloidal soap than by the fiber of cloth or by the skin.

517. Glycerin ($C_3H_5(OH)_3$). This is a colorless oily liquid having a sweet taste. Nitric acid reacts with it just as with a base, forming the nitrate $C_3H_5(NO_3)_3$:

$$C_3H_5(OH)_3 + 3\ HNO_3 \longrightarrow C_3H_5(NO_3)_3 + 3\ HOH$$

The nitric acid used in this reaction is mixed with a little sulfuric acid, the latter serving to absorb the water produced. The resulting nitrate is a slightly yellowish oil commonly known as *nitroglycerin.*

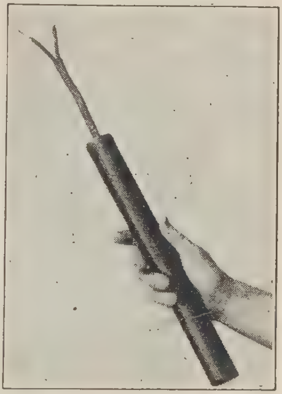


FIG. 239. A stick of dynamite with fuse attached

Nitroglycerin is very explosive. This is because the compound is very unstable and yields on decomposition a large volume of gases, chiefly carbon dioxide, nitrogen, and oxygen. One volume of the liquid gives about 1300 volumes of these gases, which is expanded by the heat of the reaction to more than 10,000 volumes; hence the great force of the explosion. Dynamite consists of nitroglycerin absorbed in wood pulp together with some oxidizing agent (Fig. 239). It is not so easily exploded as pure nitroglycerin, and is used more largely because it can be shipped with safety.

VI. Coal-Tar Compounds

518. ***Introduction.*** We have all heard of coal-tar compounds, coal-tar dyes, coal-tar medicines. What is the nature of these compounds, and for what are they used?

When studying the manufacture of coal gas (§ 464), we learned that when coal is heated in the absence of air there are formed coke, coal gas, ammonia, and a thick tarry mass known as *coal tar.* In the early days of coal gas this tar proved a nuisance and had to be disposed of at great expense. Chemists began to study this material and as a result coal tar now furnishes us with thousands of useful compounds — dyes, medicines, disinfectants, explosives. Thus the chemist has been able to turn a less than useless substance into compounds of the greatest importance to our welfare.

The process of refining coal tar (that is, separating it into its constituents) is much the same as that used in refining petroleum (§ 451). The tar is heated in large iron stills; the different products distill over in the general order of their boiling points.

519. Composition of coal tar. Coal tar is a very complex mixture of compounds, colored black with finely divided carbon. Most of these compounds are present in small percentages, so that it pays to separate only a few of them — not more than a dozen. The six most important of these are shown in Fig. 240. Each of these compounds, however, serves as the *source material* for the preparation of other compounds, and these in turn for still others. *All these compounds, whether present in coal tar or prepared from those that are present in coal tar, are known collectively as coal-tar compounds.* Many thousands of them are known.

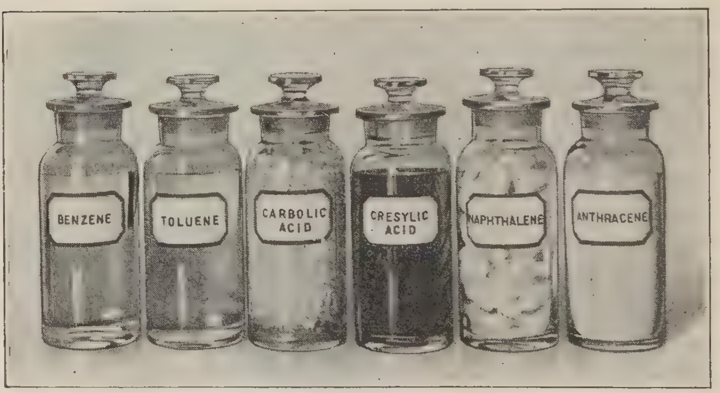


FIG. 240. Some of the principal constituents obtained directly from coal tar

The chart (Fig. 241) gives us some idea of the kinds of compounds that are derived from coal tar and also the relation of the compounds to each other. Thus, *toluene* is obtained directly from coal tar, as indicated by the arrow, while from toluene (following the arrows) we obtain benzoic

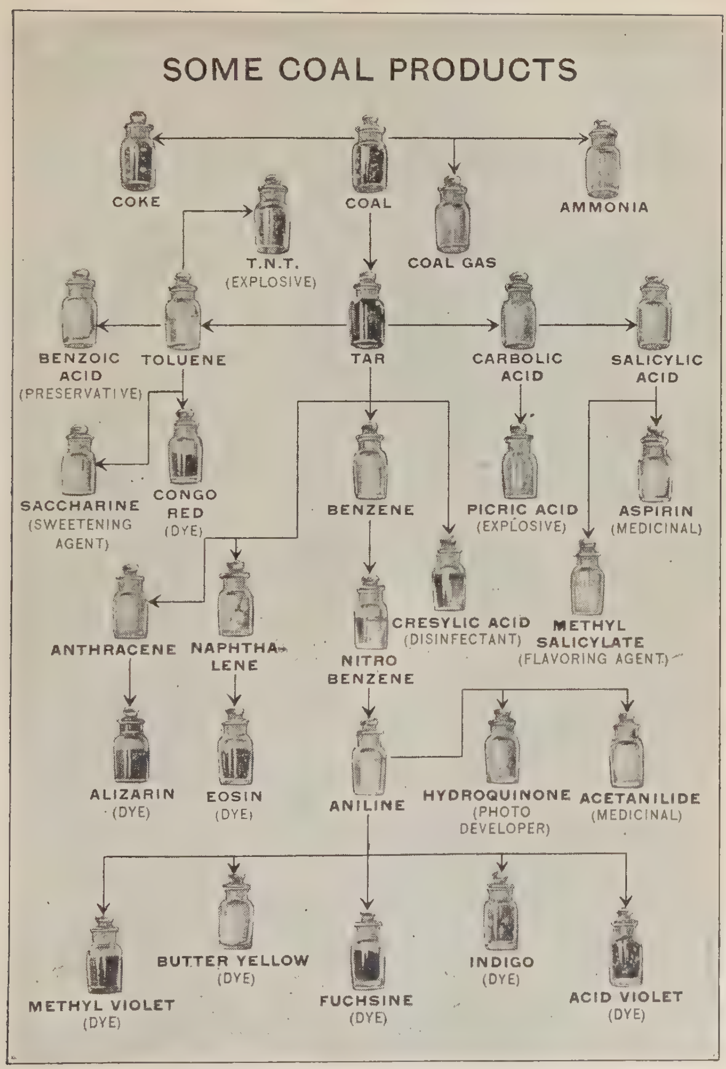

SOME COAL PRODUCTS
COKE
COAL
AMMONIA
COAL GAS
T.N.T. (EXPLOSIVE)
BENZOIC ACID (PRESERVATIVE)
TOLUENE
TAR
CARBOLIC ACID
SALICYLIC ACID
SACCHARINE (SWEETENING AGENT)
CONGO RED (DYE)
BENZENE
PICRIC ACID (EXPLOSIVE)
ASPIRIN (MEDICINAL)
ANTHRACENE
NAPHTHALENE
NITRO BENZENE
CRESYLIC ACID (DISINFECTANT)
METHYL SALICYLATE (FLAVORING AGENT)
ALIZARIN (DYE)
EOSIN (DYE)
ANILINE
HYDROQUINONE (PHOTO DEVELOPER)
ACETANILIDE (MEDICINAL)
METHYL VIOLET (DYE)
BUTTER YELLOW (DYE)
FUCHSINE (DYE)
INDIGO (DYE)
ACID VIOLET (DYE)

FIG. 241. Chart showing the derivation of some coal-tar compounds

acid, trinitrotoluene (T.N.T.), saccharine, and Congo red. Following the arrows backward we can trace the *ancestry* of each compound. The dyes at the bottom of the chart are all derived from aniline, but aniline is prepared from nitrobenzene, and this from benzene, and benzene from coal tar.

520. Properties and uses of some important coal-tar compounds. It is possible to mention here only a few of the individual coal-tar compounds. We shall describe six compounds (Fig. 240) obtained directly from coal tar and a few typical compounds derived from each.

1. ***Benzene*** **(C_6H_6).** This is a colorless, highly inflammable liquid boiling at 79.6°. When treated with nitric acid, *nitrobenzene* ($C_6H_5NO_2$) is formed, and this, on reduction, yields a nearly colorless liquid known as *aniline* ($C_6H_5NH_2$), from which hundreds of dyes of all colors are prepared.

2. ***Toluene*** **(C_7H_8).** This resembles benzene in appearance. When treated with nitric acid, it forms the solid compound *trinitrotoluene* (T.N.T.), so largely used as an explosive in the World War. From toluene there are also prepared *saccharine,* a compound five hundred times as sweet as sugar, and *benzoic acid,* whose sodium salt, *sodium benzoate,* is used as a food preservative.

3. ***Carbolic acid (phenol)*** **(C_6H_5OH).** The pure acid is a white solid and is very poisonous. It serves for the preparation of *salicylic acid,* from which is prepared the well-known medicine *aspirin.* Carbolic acid is also used in the preparation of *picric acid* (a valuable explosive) and such substances as *bakelite* and *condensite,* used for making umbrella handles, pipestems, buttons, phonograph records, insulators in electrical devices, and many similar articles.

4. ***Cresylic acid*** **(C_7H_7OH).** This substance is the basis of nearly all the common disinfectants used in our homes for such purposes as cleansing drainpipes and sinks.

5. ***Naphthalene*** **($C_{10}H_8$).** This is a white crystalline compound, best known to us in the form of *moth balls.*

6. ***Anthracene*** **($C_{14}H_{10}$).** This is a nearly white solid and serves for the preparation of *alizarin,* one of our most valuable dyes.

521. Coal-tar dyes. All dyes derived from coal tar are known as *coal-tar* or *aniline dyes.* The first aniline dye was made in 1856 by William Perkin (Fig. 6), an English boy, seventeen years of age. This led to the discovery of others, until now many hundreds of these dyes are known, of every imaginable color. It is interesting to note that two of the most common, namely, *indigo* and *alizarin,* were formerly obtained from vegetable sources. Chemists found out how to make them in the laboratory, and now they are made in this way at a much lower cost than formerly. The method of dyeing will be discussed in a later chapter.

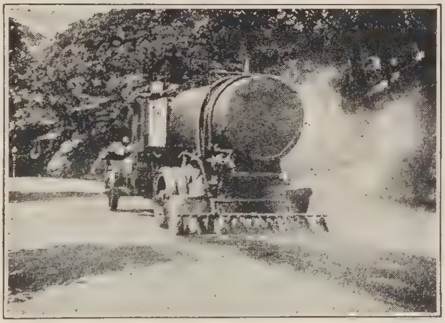


FIG. 242. Using pitch obtained from coal tar in road construction

Before the World War nearly all our dyes came from Germany. During the war this supply was cut off, and there was a temporary shortage of dyes. American chemists soon solved the problem connected with their production, and now the United States produces an adequate supply of dyes of the very highest grade.

522. Pitch and its uses. When coal tar is distilled there remains in the still a very thick, viscous, tarry mass known as *pitch,* which has extensive uses in road construction. Pitch is frequently sprinkled on roadways as a binder to prevent the wearing away of the road (Fig. 242).

SUMMARY OF PARTS IV, V, AND VI OF CHAPTER, IN QUESTION FORM

1. Name, and give formula of, an organic acid that is (*a*) a liquid present in vinegar; (*b*) a white crystalline solid, an acid salt of which occurs in grapes; (*c*) a white amorphous solid, a derivative of which occurs in fats.

2. When the missing words are supplied, the following paragraph describes the chemical change that occurs in the manufacture of cider vinegar:

The ______ in the apple juice first undergoes a chemical change known as ______ ______, the products of which are ______ and ______. The ______ thus formed is then oxidized to a compound called ______ ______, and the chemical change is known as ______ ______.

3. How can you tell cider vinegar from distilled vinegar?

4. Give the name of the class of compounds formed by displacing the hydrogen of an acid by (*a*) a metal; (*b*) a hydrocarbon radical.

5. Complete the following table, which refers to the acids whose derivatives are present in oils and fats:

NAME	FORMULA	NAME OF ESTER PRESENT IN FATS	FORMULA OF ESTER PRESENT IN FATS
1.			
2.			
3.			

6. Name the food substance for which each of the following are suitable substitutes: (*a*) refined corn oil and cottonseed oil; (*b*) oleomargarine; (*c*) hydrogenated cottonseed oil.

7. What is the common name for a mixture of the sodium salts of palmitic, oleic, and stearic acids?

8. Name (*a*) the materials used in the manufacture of soap; (*b*) also the compound formed along with the soap.

9. (*a*) Write the equation for the reaction that takes place when a solution of calcium chloride is added to a solution of soap. (*b*) What well-known fact is due to this chemical change?

10. Name three substances that together constitute dynamite.

11. Inspect Fig. 241, and select four substances that are formed by heating coal in closed retorts.

12. What name is given to the process that is referred to in question 11 (§ 159, 1)?

13. Inspect Fig. 241, and select a compound obtained from coal tar which serves for the preparation of all four of the following: a dye; a preservative; an explosive; a sweetening agent.

14. In Fig. 241, trace the steps in obtaining aspirin from coal.

15. Name two dyes formerly obtained from vegetable sources that are now prepared from coal tar.

THOUGHT QUESTIONS

1. (*a*) Why do we color butter? (*b*) Why do we color oleomargarine? (*c*) Why do some states forbid the coloring of oleomargarine? (*d*) Do you think that a law forbidding the coloring of oleomargarine can be justified?

2. (*a*) What is the difference in composition between benzene and benzine? (*b*) Give the source of each. (*c*) What properties have they in common?

3. An industrial concern which manufactures explosives in times of war would probably manufacture what substances in times of peace? (Answer by reference to Fig. 241.)

FOR HONOR STUDENTS

1. Select one of the following readings and write a theme on the subject, or report verbally to the class in case the teacher so desires: Chapter XXI (entitled "Soap — Cleanliness through Chemistry") in Volume II of "Chemistry in Industry"; Chapter IV (entitled "Coal-tar Colors") in "Creative Chemistry."

2. Obtain samples of different kinds of vinegars, evaporate about 50 cc. of each to dryness on a water bath, and examine the residues. Exhibit the results to the class.

VII. Foods

523. *Introduction.* While the compounds present in our foods are very numerous and many of them exceedingly complex, yet all of them may be included under a few general heads, namely, *proteins, fats, carbohydrates, mineral matter, vitamins, water,* and *oxygen.* The first four of these are often referred to collectively as *nutrients.* Water and oxygen are not usually thought of as food; nevertheless, both are essential, since water constitutes about two thirds of the body and oxygen is necessary to oxidize the organic matter of the diet and to liberate energy.

We have already studied the fats, the carbohydrates, water, and oxygen, and are familiar with their composition and properties. The *proteins* are complex compounds of nitrogen that are essential constituents of both plants and animals so that there is no life without them. The term *mineral matter* includes the compounds of the metals, such as calcium phosphate ($Ca_3(PO_4)_2$), which is the chief constituent of our bones, and salt. Since the mineral matter is left as a residue when foods are burned, it is customary to report it as *ash* in giving the analysis of foods. The composition of many of our foods is given on page 410.

524. The vitamins. The term *vitamin* is applied to a number of substances occurring in many of our foods in variable amounts but always in very small percentages. They have not been isolated in a perfectly pure condition, so that little is known concerning their constitution; they do not appear to belong to any single class of substances. All the vitamins are more or less unstable at the temperature of boiling water, especially where air or oxygen is present.

At least six kinds of vitamins are known to exist, and a proper distribution of these bodies in our food is essential to a nourishing diet. The name and function of each, together with some foods rich in each, are as follows:

1. ***Vitamin A.*** Promotes growth, keeps the body in good condition, and prevents certain eye diseases. Present especially in liver, butter, cheese, eggs, green-leaf vegetables such as spinach and lettuce. cod-liver oil, and carrots.

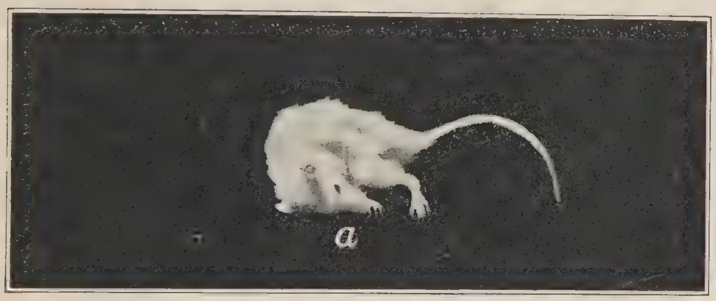


FIG. 243. Effect of deficiency of vitamin B in diet of a rat

At twenty-eight days of age the rat was placed on a diet containing but a minimum of vitamin B. It lost weight rapidly and developed paralysis as in *a*

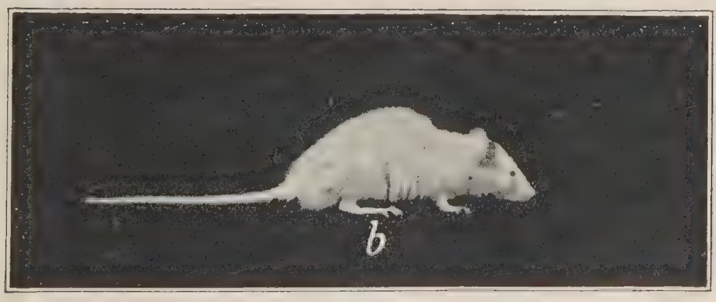


FIG. 244. Effect of renewed supply of vitamin B

A food rich in vitamin B was then fed to the rat; after twenty-four hours the symptoms of paralysis had entirely disappeared, and it appeared as in *b*. (Photographs from the United States Department of Agriculture)

2. ***Vitamin B.*** This vitamin improves the appetite and prevents certain nerve diseases which cause a form of paralysis (see Figs. 243, 244). Present in the outer layer of cereals and in asparagus, tomatoes, peas, and yeast.

3. ***Vitamin C.*** Prevents scurvy. Present in oranges, lemons, grapefruit, raw cabbage, apples, and tomatoes.

4. ***Vitamin D.*** Prevents rickets. Present in cod-liver oil. It is also formed in the tissues of our bodies when we are exposed to sunlight or to ultraviolet rays (Fig. 127).

5. ***Vitamin E.*** Necessary for reproduction and growth of young animals. Present in wheat germs and in lettuce.

6. ***Vitamin G.*** Prevents certain skin diseases. Present in milk, eggs, meat, yeast, and green vegetables.

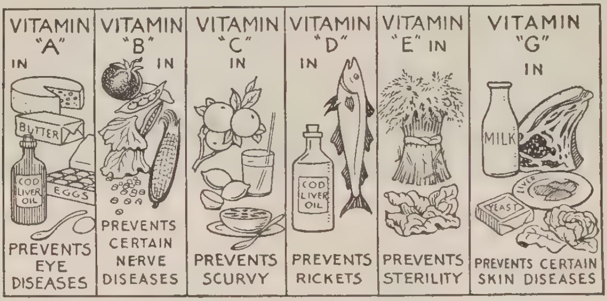

VITAMIN "A" IN
BUTTER
COD LIVER OIL
EGGS
PREVENTS EYE DISEASES
VITAMIN "B" IN
PREVENTS CERTAIN NERVE DISEASES
VITAMIN "C" IN
PREVENTS SCURVY
VITAMIN "D" IN
COD LIVER OIL
PREVENTS RICKETS
VITAMIN "E" IN
PREVENTS STERILITY
VITAMIN "G" IN
MILK
LIVER
YEAST
PREVENTS CERTAIN SKIN DISEASES

FIG. 245. Sources of vitamins. (Drawing after *Science News Letter*)

All the above are present to a certain extent in milk and in green vegetables, especially in lettuce and spinach (Fig. 245). Just how these vitamins act to promote growth and prevent disease is not known.

525. The functions of foods. The functions of foods are stated in brief form in the chart on page 409. The facts included in this chart are of great importance and should be carefully studied.

While the proteins, fats, and carbohydrates are to a certain extent interchangeable, experiments show that a proper mixture of these materials is essential to health. Of course it is true that one can live for many days on a purely protein diet or on a diet purely of fats and carbohydrates; in fact, persons can live for many days without any food whatever other than water. In all such cases the body derives the necessary materials from the surplus supply always stored up in the normal body.

FUNCTIONS OF FOODS[1]

FOOD CONSTITUENT	FUNCTION	OCCURS ABUNDANTLY IN
Proteins . . .	Build muscle and other organs. Supply fuel for the body	Meat, eggs, milk, cereals
Fats	Supply fuel for the body	Butter, lard, vegetable oils
Carbohydrates	Supply fuel for the body	Sugar, starch, cereals
Minerals . .	Build bone and blood; regulate such body processes as clotting of blood, activity of muscles and nerves, and oxidation. Assist in digestion	Milk, eggs, green leaves, meat, cereals, fruits and vegetables
Vitamins . .	Stimulate digestive organs and growth, control deposition of bone, maintain a healthy condition of skin and blood-vessel walls	Green leaves, milk, eggs, meat, cereals, fruits, tubers, etc.
Oxygen . . .	Oxidation in body liberates energy for work, heat, etc.	Atmosphere
Water	Solvent, body constituent. Gives fluidity to blood. Regulates body temperature, etc.	Wells, rivers, lakes

526. Energy value of foods. Experiments show that the heat of the body, as well as the energy used in muscular work, results from the oxidation of food. When eaten, food undergoes complex changes in which the insoluble portions are converted into soluble compounds. These are absorbed into the system and then either undergo oxidation directly or are temporarily built into tissues which later undergo oxidation. In this process most of the carbon is finally changed into carbon dioxide and exhaled from the lungs, while the hydrogen is changed into water. The nitrogen is excreted largely in the form of urea ($CO(NH_2)_2$).

Broadly speaking, foods may be regarded as fuel from the oxidation of which in the body the energy necessary for physical requirements is set free. In the study of foods it is

---

[1] Food is that which, taken into the body, builds tissue or yields energy.

AVERAGE COMPOSITION OF EDIBLE PORTION OF TYPICAL FOODS EXPRESSED IN GRAMS PER 100 GRAMS OF FOOD

Food	Water	Protein	Fat	Carbohydrate	Ash	Fuel Value (Cal. per 100 g.)
Almonds	4.8	21.0	54.9	17.3	2.0	647
Apples	84.6	0.4	0.5	14.2	0.3	63
Asparagus	94.0	1.8	0.2	3.3	0.7	22
Bacon (smoked)	20.2	9.9	64.8	—	5.1	623
Bananas	75.3	1.3	0.6	22.0	0.8	99
Beans (dried)	12.6	22.5	1.8	59.6	3.5	345
Beans (string)	89.2	2.3	0.3	7.4	0.8	42
Beef (lean steak)	70.0	21.0	7.9	—	1.1	155
Beef (slightly fat)	73.8	22.1	2.9	—	1.2	115
Beets	87.5	1.6	0.1	9.7	1.1	46
Bread (corn)	38.9	7.9	4.7	46.3	2.2	259
Bread (graham)	35.7	8.9	1.8	52.1	1.5	260
Bread (white)	35.3	9.2	1.3	53.1	1.1	260
Butter	11.0	1.0	85.0	—	3.0	769
Cabbage	91.5	1.6	0.3	5.6	1.0	32
Carrots	88.2	1.1	0.4	9.3	1.0	45
Celery	94.5	1.1	0.1	3.3	1.0	19
Chestnuts	45.0	6.2	5.4	42.1	1.3	242
Chicken	63.7	19.3	16.3	—	1.0	224
Codfish (fresh)	82.6	15.8	0.4	—	1.2	67
Corn (green)	75.4	3.1	1.1	19.7	0.7	101
Dates	13.8	1.9	2.5	70.6	1.2	313
Eggs	73.7	14.8	10.5	—	1.0	154
Figs	18.8	4.3	0.3	74.2	2.4	317
Ham (lean, smoked)	53.5	20.2	20.8	—	5.5	268
Lettuce	94.7	1.2	0.3	2.0	0.9	16
Macaroni	78.4	3.0	1.5	15.8	1.3	89
Milk	87.0	3.3	4.0	5.0	0.7	69
Oatmeal	7.3	16.1	7.2	67.5	1.9	400
Olive oil	—	—	100.0	—	—	900
Oranges	86.9	0.8	0.2	11.6	0.5	51
Peaches	89.4	0.7	0.1	9.4	0.4	41
Peanuts	9.2	25.8	38.6	24.4	2.0	548
Peas (green)	74.6	7.0	0.5	16.9	1.0	100
Plums	78.4	1.0	—	20.1	0.5	84
Potatoes	78.3	2.2	0.1	18.4	1.0	83
Prunes (dried)	22.3	2.1	—	73.3	2.3	302
Raisins	14.6	2.6	3.3	76.1	3.4	345
Rice	12.3	8.0	0.3	79.0	0.4	351
Salmon	64.6	21.2	12.8	—	1.4	200
Spinach	92.3	2.1	0.3	3.2	2.1	24
Strawberries	90.4	1.0	0.6	7.4	0.6	39
Tomatoes	94.3	0.9	0.4	3.9	0.5	23
Turnips	89.6	1.3	0.2	8.1	0.8	40
Wheat flour	11.9	13.3	1.5	72.7	0.6	357

These values are taken from *Bulletin No. 28*, office of Experiment Station, Washington, D.C. The fuel values are obtained from the following formula:

Cal. in 100 g. $= 4\,P + 9\,F + 4\,C$, in which P, F, and C represent respectively the number of grams of protein, fat, and carbohydrates in 100 g. of the food.

convenient, therefore, to use their *fuel values* (heats of combustion) as a basis of comparison. These values are determined in the calorimeter (Fig. 202) and expressed in large calories (represented by the abbreviation Cal.), which are 1000 times as large as the small calorie (cal.).

Now experiments show that the body obtains from each of the three classes of foods, when absorbed in the system and oxidized, approximately the following fuel values:

CLASS OF FOODS	CALORIES PER GRAM	CALORIES PER POUND
Carbohydrates	4	1815
Fats	9	4082
Proteins	4	1815

527. Amount and nature of foods necessary for health. Many studies have been made in order to find out just how much and what kind of food is best adapted for the preservation of health. Evidently many conditions, such as one's age, weight, and occupation and the climate in which one lives, enter into the problem. In summer, for example, we live more largely on fruits and other foods rich in water content since these have little fuel value, while in winter we crave foods rich in fats and carbohydrates.

Since the fats and carbohydrates have nearly the same function, it is sufficient in stating food requirements for a period of, say, twenty-four hours to give simply the weight of protein necessary, together with the total fuel value. The difference between the total fuel value and that of the required protein gives the number of calories to be supplied from fats and carbohydrates. Such a mixture of these two food materials is selected that the fuel value of the mixture, together with the fuel value of the protein, equals the total fuel value required. Different dietary standards have been proposed, but the following ones (p. 412), given by Atwater, are generally accepted. They give the food requirements for a period of twenty-four hours.

CHARACTER OF INDIVIDUAL	PROTEINS REQUIRED	FUEL VALUE REQUIRED
Man with very hard muscular work (woodchopper, football player)	175 g.	5500 Cal.
Man with moderately active muscular work	125 g.	3400 Cal.
Man with light to moderate muscular work	112 g.	3050 Cal.
Man at sedentary occupation or woman with moderately active work	100 g.	2700 Cal.
Man at rest or woman with light muscular work	90 g.	2450 Cal.
Boy 15 to 16 years	108 g.	3060 Cal.
Boy 13 to 14 years or girl 15 to 16	100 g.	2700 Cal.
Boy 12 to 13 years or girl 14 to 15	87 g.	2380 Cal.
Boy 10 to 11 years or girl 10 to 12	75 g.	2040 Cal.
Boy 6 to 9 years	62 g.	1700 Cal.

In selecting our foods, however, it is not only essential that we secure the proper proportion of protein, fats, carbohydrates, and mineral matter, but we must also consider

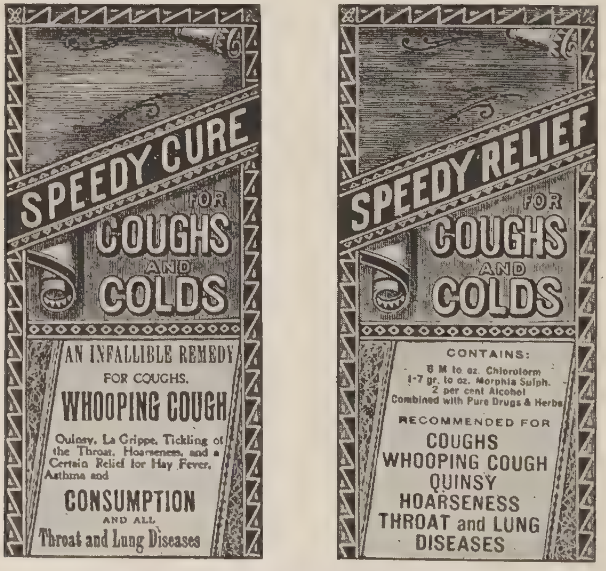

SPEEDY CURE
FOR
COUGHS
AND
COLDS
AN INFALLIBLE REMEDY
FOR COUGHS.
WHOOPING COUGH
Quinsy, La Grippe, Tickling of the Throat, Hoarseness, and a Certain Relief for Hay Fever, Asthma and
CONSUMPTION
AND ALL
Throat and Lung Diseases
SPEEDY RELIEF
FOR
COUGHS
AND
COLDS
CONTAINS:
8 M to oz. Chloroform
1-7 gr. to oz. Morphia Sulph.
2 per cent Alcohol
Combined with Pure Drugs & Herbs
RECOMMENDED FOR
COUGHS
WHOOPING COUGH
QUINSY
HOARSENESS
THROAT and LUNG
DISEASES

FIG. 246. The label on a well-known patent medicine before and after the passage of the Pure Food and Drugs Act

whether the foods selected contain these ingredients in a palatable and digestible condition. Especially must we make such a selection as will furnish us with the necessary vitamins; in other words, *we must take into consideration quality as well as quantity of food.* For these reasons some foods, such as milk, may not seem to rank high as economical foods considered simply from their content of fat, carbohydrates, and protein; yet when we take into account the character of these constituents present in milk and especially its vitamin and mineral content, its effect in maintaining health as well as in nourishing the body makes it one of our most valuable foods.

528. Pure Food and Drugs Act. In 1906 the Federal Congress passed what is known as the Pure Food and Drugs Act. This fixes the standard of various foods and drugs, and prescribes that all labels must tell the truth and must state the presence of any dangerous or habit-forming drugs. The effect of the act may be seen by a study of Fig. 246, which shows the label used on a well-known patent medicine before the act was passed and also how it had to be modified to meet the requirements of the act.

SUMMARY OF PART VII OF CHAPTER, IN QUESTION FORM

1. Name the nutrients.

2. Referring to the chart on page 409, answer the following questions:
   (*a*) What is food?
   (*b*) Food as purchased contains what substances?
   (*c*) Name food substances rich in protein.
   (*d*) Name food substances rich in fats.
   (*e*) Name food substances rich in carbohydrates.
   (*f*) Name the special function of each of the nutrients.
   (*g*) What common function have protein, fats, and carbohydrates?

3. One of the purposes for which food is taken into the body is to release energy. (*a*) Through what chemical process is the energy released? (*b*) Name two products of the reaction. (*c*) Which nutrient releases energy in relatively large amounts? (*d*) What unit is used to measure the fuel values of food?

4. Consult page 412 and note the number of calories per day you need.

5. Name the nutrient and the vitamin present in abundance in each of the following foods: (*a*) bread; (*b*) butter; (*c*) meat; (*d*) tomatoes.

6. Why do we associate certain foods, such as bread and butter, ham and eggs, oatmeal and cream? (Consult the table on page 409.)

7. What weight of water are you buying when you buy 10 lb. of (*a*) apples? (*b*) string beans? (*c*) butter? (*d*) peaches? (*e*) spinach? (*f*) celery? (*g*) tomatoes?

8. What action did the Federal government take in 1906 to aid you in improving your diet and your health?

FOR HONOR STUDENTS

Read one of the following chapters in "Chemistry in Agriculture" and write a theme on the subject, reporting items of interest to the class: (*a*) Chapter II, entitled "The World's Food Factory, or the Plant in Air and Light"; (*b*) Chapter VI, entitled "Cereals"; (*c*) Chapter VIII, entitled "Fruits and Vegetables"; (*d*) Chapter XII, entitled "Vitamins in Human and Animal Nutrition."

CHAPTER XXXV

THE METALS

The Main Supports of an Industrial Age

529. *Introduction.* To almost anyone the word *metal* brings up a clear idea that does not seem to need explanation or definition. Iron, copper, lead, gold, silver, have been used by men since the childhood of the race, and each of us will recognize any one of them by sight. There are, however, many important metals that most people have never seen; and some of them are light in weight, easily melted, soft enough to be cut with a knife, and in very few ways resemble the familiar metals.

The chemical characteristics of most of the metals are much less well known to the average person than is their general appearance. Beyond the fact that some of them rust in air and some are easily attacked by acids, he knows little about them.

We must first get a clear idea of these interesting elements *as a group*, and then go rapidly over the individual peculiarities and the most useful compounds of some of the most important of the metals.

530. Properties of the metals. At ordinary temperature the metals are all solids, except mercury, which is a liquid. Most metals have a high density, are good conductors of heat and electricity, are notably crystalline in structure, and take a high polish. With the exception of gold and copper they have a silvery luster.

531. Chemistry of the metals. Most of the metals combine readily with oxygen, sulfur, or chlorine, and their surface tarnishes quickly on exposure to the air. Those that do not tarnish, such as gold and silver, are sometimes called *noble* metals. Those metals above hydrogen in the electrochemical series act upon dilute acids and liberate hydrogen. Those below hydrogen do not, but many of them are first oxidized by acids and the oxides then dissolve in the acids and form salts (§ 295, 3; § 347, 3).

The hydroxides of the metals are *bases*, and from a chemical point of view *we may define a metal as an element whose hydroxide is a base.* When the hydroxide of a metal or any of its ordinary salts are dissolved in water, the metal atom becomes a simple positive ion. We may then say that *a metal is an element whose atoms form positive ions in solution.* This definition classes hydrogen as a metal, and in a chemical way it acts as one. The atoms of hydrogen and of the metals have few electrons in their valence orbits, and tend to lose these easily, forming positive ions.

532. Alloys of metals. A few of the metals find large uses in very pure form, such as copper, aluminum, lead, and tin. A vast amount of *nearly* pure iron is used but, as we shall see, it is necessary to have certain impurities present in order that the iron may have the properties we usually want it to have. In the great majority of cases the metallic objects with which we are familiar are not made of *one* metal, but of alloys of two or more metals. For example, gold jewelry, silver plate, coins of all kinds, brass, bronze, pewter, most objects of iron (such as automobile parts, Fig. 247), are alloys. More and more inventors and manufacturers want metal bodies of very definite properties possessed by no one metal but possible to get in alloys. Some large firms do nothing but manufacture alloys guaranteed to have almost any specified properties, — they make metals to order. Naturally they make them as cheaply as possible to serve the special purpose in view; so alloys vary greatly in composition.

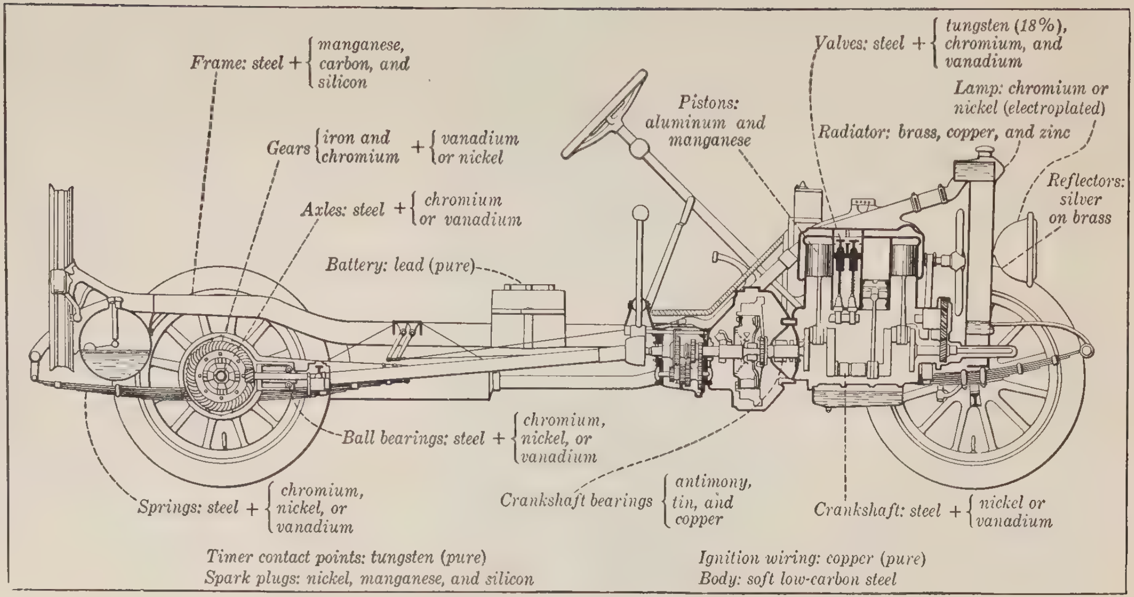

Frame: steel + { manganese, carbon, and silicon
Gears { iron and chromium + { vanadium or nickel
Axles: steel + { chromium or vanadium
Battery: lead (pure)
Pistons: aluminum and manganese
Valves: steel + { tungsten (18%), chromium, and vanadium
Lamp: chromium or nickel (electroplated)
Radiator: brass, copper, and zinc
Reflectors: silver on brass
Ball bearings: steel + { chromium, nickel, or vanadium
Springs: steel + { chromium, nickel, or vanadium
Crankshaft bearings { antimony, tin, and copper
Crankshaft: steel + { nickel or vanadium
Timer contact points: tungsten (pure)
Spark plugs: nickel, manganese, and silicon
Ignition wiring: copper (pure)
Body: soft low-carbon steel

FIG. 247. Some alloys used in an automobile

533. Metallurgy. A few of the least active of the metals, such as gold and copper, occur to some extent in nature in the native state. Most of them are found in combination as *oxides*, as *sulfides*, or as salts of various acids, especially as silicates. The process of winning a metal from the mineral in which it occurs is called *metallurgy*. Not every mineral is suited to the profitable extraction of the metal which it contains. Thus, there is a high percentage of aluminum in clay, but as yet the metal cannot be obtained cheaply from that source. A mineral suited to the commercial production of a metal is called an *ore* of that metal. The details of the metallurgy of any given metal must be adapted to the properties of the metal, to the ores available, and to the cost of the operation.

534. Roasting. Most metals that occur in nature as oxides are obtained from their ores by reduction with carbon. As they are dug from the mines, most oxide ores contain some sulfides, water, and carbon dioxide in the form of carbonates. Before reduction with carbon, these ores are heated in open furnaces with free access of air. This oxidizes the sulfur to sulfur dioxide, and this gas, along with the water and the carbon dioxide, is driven off; at the same time the metal is converted to its oxide. This preliminary treatment of the ore is called *roasting*.

535. Flotation. Most of the heavier metals, such as zinc, copper, lead, silver, and gold, are found either as sulfides or as native metals. The rich deposits of the world have become largely exhausted, and it is now necessary to use low-grade ores — often containing as little as 1 per cent of the desired metal. These ores must be crushed and the valuable portion *concentrated* before the metals can be obtained from them.

The most ingenious and effective way of doing this is called *flotation*. The finely crushed ore is churned up into a froth with water and a little oil — often pine oil. Although the particles of sulfides or of metals are much heavier than either water or the powdered rock, they stick to the bubbles of froth, and are *floated* off with the froth into settling-basins, from which a very concentrated ore is recovered for reduction. The flotation process cannot be used to concentrate *oxide* ores, for oxides do not float in the froth. Were it not for this flotation process the heavy-metal industries would be in a bad way, for it would not pay to work most of our mines without it. With it, old dump piles yield large values.

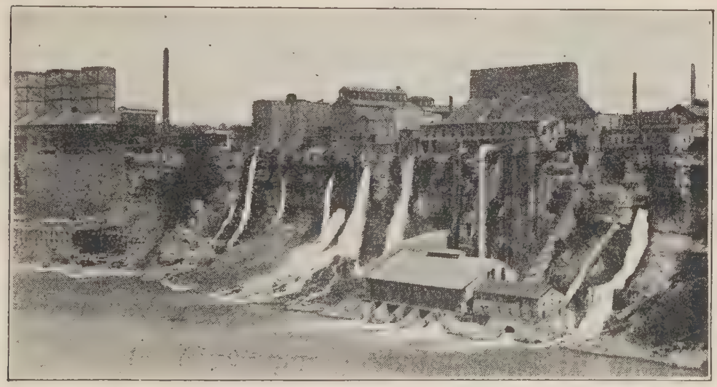


FIG. 248. Electrochemical power plants at Niagara Falls

536. Electrochemical industries. To an ever-increasing extent electrical energy is being used both in the separation and refining of the metals and for the production of many compounds. In a number of instances mention of such methods has already been made. Naturally these industries tend to develop most extensively in localities where water power is abundant. Norway has many electrochemical industries. Those of the United States and Canada center at Niagara Falls, the extensive power plants being shown in Fig. 248.

537. Compounds of the metals. Since the metallic elements are base-forming elements, the compounds which they form are chiefly oxides, hydroxides, and salts of various acids. We have seen (§ 238) that the number of salts is very large. It will be possible for us to study only the most important of these. With very few exceptions the compounds of the metals are crystalline solids.

538. Preparation of salts. There are two general ways of preparing salts which are employed so often that it is well to fix them in mind at the outset of the study of metals.

1. ***Soluble salts.*** If a given salt is *soluble* it can usually be prepared in solution by treating the proper metal, or its oxide, hydroxide, or carbonate, with the proper acid. All these reactions have already been illustrated repeatedly:

$$\begin{aligned}
Zn + H_2SO_4 &\longrightarrow ZnSO_4 + \overline{H_2} && (\S\,152)\\
CuO + H_2SO_4 &\longrightarrow CuSO_4 + H_2O && (\S\,347,\ 3)\\
NaOH + HCl &\longrightarrow NaCl + H_2O && (\S\,237)\\
CaCO_3 + 2\ HCl &\longrightarrow CaCl_2 + H_2O + \overline{CO_2} && (\S\,165)
\end{aligned}$$

2. ***Insoluble salts.*** A very large number of salts are insoluble in water, and these can be made by *precipitation.* All that it is necessary to do is to bring together in solution two salts, one of which will supply the desired metallic ion and the other the negatively charged ion. If, for example, it is known that silver chloride is insoluble in water, it is to be expected that this salt will be precipitated on mixing a solution of any silver salt, such as silver nitrate, with that of any chloride, such as sodium chloride, thus:

$$Ag^+, NO_3^- + Na^+, Cl^- \longrightarrow \underline{AgCl} + Na^+, NO_3^-$$

539. Solubility of salts and hydroxides. It will be seen that a knowledge of the solubility of various salts is of great importance if one wishes to devise a means of preparing a given salt. Fortunately it is possible to put into brief form the facts relating to the solubility of the common salts in water, and these rules will have constant application in the pages which follow.

1. ***Hydroxides.*** All *hydroxides are insoluble* except those of ammonium, sodium, potassium, calcium, barium, and strontium.

2. ***Nitrates.*** All *nitrates are soluble.*

3. ***Chlorides.*** All *chlorides are soluble* except silver and mercurous chlorides. (Lead chloride is soluble in hot water.)

4. ***Sulfates.*** All *sulfates are soluble* except those of lead, barium, and strontium. (Sulfates of silver and calcium are only moderately soluble.)

5. ***Sulfides.*** All *sulfides are insoluble* except those of ammonium, sodium, and potassium. The sulfides of calcium, barium, strontium, and magnesium are insoluble in water, but are changed by water into acid sulfides which are soluble; so they cannot be prepared by precipitation.

6. ***Carbonates, phosphates, and silicates.*** All normal *carbonates, phosphates, and silicates are insoluble* except those of ammonium, sodium, and potassium.

540. Ionic tests. Familiarity with the solubility of all the different salts, both in water and in acids, makes it possible to work out a system of tests for the various ions, both negative and positive. Thus we have found (§ 349) that since barium sulfate is insoluble both in water and in acids, the addition of barium ions (Ba^{++}) to a solution will always cause a white precipitate of barium sulfate if sulfate ions (SO_4^{--}) are present. Silver ions (Ag^+) will precipitate insoluble silver chloride from a solution in which chlorine ions (Cl^-) are present (§ 315).

In like manner it will be seen that if we add a soluble hydroxide (OH^- ions) to a solution, all those metals whose hydroxides are insoluble will form precipitates (all save NH_4, Na, K, Ca, Sr, Ba). If we get a precipitate, we must devise other ion reactions to identify the particular ions present. A systematic scheme of this kind which provides for the identification of all the common ions, both positive and negative, is called *qualitative analysis*.

CHAPTER SUMMARY IN QUESTION FORM

1. Mention four properties that characterize most of the metals.

2. What name do we give to those elements whose hydroxides are bases?

3. What kind of ions do metals form when their salts are dissolved in water?

4. Hydrogen is similar to metals in what two respects?

5. Most of the metals are found in nature in combination (*a*) with what elements, or (*b*) with what acid radicals?

6. What name is given to minerals from which metals can be profitably extracted?

7. Are most of the metallic objects with which you are familiar pure metals or mixtures of metals?

8. What advantage do mixtures of metals often have over pure metals?

9. What name do we give to the process of obtaining metals from their ores?

10. Supply the missing words: Most metals can be obtained from their ______ by first ______ them. The metals are thus converted into ______, which are then reduced with ______.

11. (*a*) Describe the process known as flotation. (*b*) What is the advantage of this process?

12. (*a*) Name a source of energy other than heat that is used extensively in metallurgy, and (*b*) name two localities where a large supply of such energy is available.

13. Illustrate by example the general method used for preparing (*a*) a soluble salt; (*b*) an insoluble salt.

14. What classes of salts are (*a*) all soluble? (*b*) nearly all soluble? (*c*) nearly all insoluble?

15. Using the proper signs to indicate ions and insoluble compounds, write the equations for the reactions that occur between the following compounds in water solutions: (*a*) sodium sulfate and barium chloride; (*b*) copper sulfate and barium chloride; (*c*) sodium chloride and silver nitrate; (*d*) ferrous sulfate ($FeSO_4$) and sodium hydroxide.

THOUGHT QUESTIONS

1. (*a*) What elements are liquid at ordinary temperatures? (*b*) Which of these are metals?

2. Make a list (*a*) of the elements so far studied that are obtained pure by the use of electrical energy; (*b*) of the compounds studied that are formed by electrical energy.

3. In what way does the popular conception of a metal differ from the chemist's?

4. Give an example of each of the following: (*a*) a metal so light that it will float on water; (*b*) a heavy metal; (*c*) a metal that quickly tarnishes in air; (*d*) a metal that is not acted upon by air; (*e*) a metal that liberates hydrogen from acids; (*f*) a metal that does not liberate hydrogen from acids.

5. Write equations other than those included in this chapter to illustrate (*a*) four ways of preparing soluble salts; (*b*) one way of preparing insoluble salts. (Underscore insoluble compounds and overscore volatile compounds.)

6. (*a*) Why cannot sodium be prepared by the electrolysis of a solution of its salts? (*b*) In general, what property must a metal possess in order that it may be so produced?

7. Suppose you wished to prepare some calcium chloride for drying gases. (*a*) What compounds would you need for its preparation? (*b*) Write the equation for the reaction involved in the preparation.

FOR HONOR STUDENTS

1. Write a theme on "The Transmutation of the Metals," touching on (*a*) the belief of the alchemists, (*b*) the belief of later chemists, and (*c*) transmutation as we believe in it today.

2. Make a list of ten different metallic articles in your homes and on your person, and state which of these are pure metal and which are alloys.

3. Name ten insoluble salts (§ 539) and devise a method for the preparation of each by precipitation.

CHAPTER XXXVI

THE ALKALI METALS

Metals whose Compounds serve us Daily

541. ***Introduction.*** In the preceding chapter we learned something about the metals as a group: how they are obtained from their ores, what their general properties are, how the chemist defines them, and other important information regarding them. We shall now proceed to get acquainted more intimately with some of the individuals that make up this group, and also with the important compounds which they form. We shall begin with those metals that are commonly called the *alkali metals*, because their hydroxides are strong bases (alkalies, § 236).

The alkali metals are five in number: sodium, potassium, lithium, rubidium, and cesium. According to the periodic law there is still another undiscovered alkali metal (p. 289). They are all univalent — a fact that will help us to tell the formulas of many of their compounds. The last three of these metals are of little importance to us, and we may pass them by with mere mention of the fact that they resemble sodium and potassium in their general properties. Moreover, we have already studied sodium and potassium, together with their hydroxides (Chap. XVI), and have learned that while these two metals themselves have but few uses, their compounds are of very great importance. To realize this, it is only necessary to mention the common names of a few of them, such as salt, washing soda, baking soda, caustic soda, borax, saltpeter, and Chile saltpeter. We shall begin our study with the most familiar of all, salt.

Compounds of Sodium

542. Sodium chloride (common salt) (NaCl). We are apt to think of salt only as a substance for seasoning our foods. While this is an important use, yet the amount required for this purpose is small compared with that required for other purposes. Because it is so abundant, it is used in the preparation of nearly all the compounds that contain either sodium or chlorine. These include many substances of the highest importance to our welfare, such as soap, glass, soda, hydrochloric acid, chlorine, and bleaching powder.

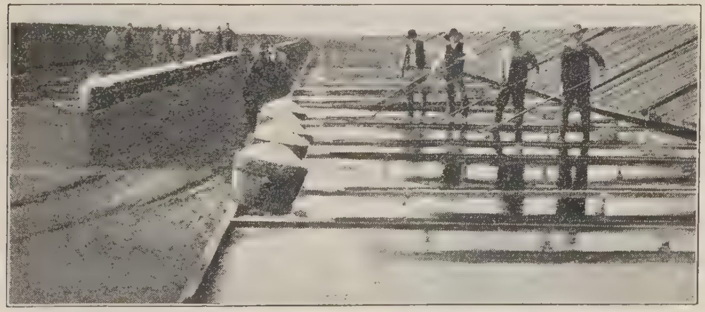


FIG. 249. The evaporation of salt brine in the open air

543. Occurrence and preparation of salt. Salt is found in nearly all natural waters, especially in the waters of the oceans and of certain lakes such as the Great Salt Lake (Utah). Thick strata of it occur in many localities, and it is mined much as coal is mined (Fig. 111). It is also obtained by digging wells into the salt deposits and pumping the solution (brine) to the earth's surface. This brine is then evaporated either by fire or, in the preparation of the coarser grades, by simply exposing it to air (Fig. 249). In the United States most of our salt comes from New York, Michigan, Ohio, Kansas, and Louisiana. In some foreign countries salt is obtained directly from sea water by evaporation.

Pure salt does not absorb moisture; the fact that ordinary salt becomes moist when exposed to air is due to the presence of impurities such as the chlorides of calcium and magnesium.

544. Sodium sulfate (Na_2SO_4). It will be recalled that hydrochloric acid is prepared by the action of sulfuric acid on sodium chloride (§ 219):

$$2\ NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2\ HCl$$

The equation tells us that whenever we make hydrochloric acid, we also make sodium sulfate. This is a white solid, readily soluble in water, and under ordinary conditions crystallizes as the hydrate, $Na_2SO_4 \cdot 10\ H_2O$, in which form it is often called *Glauber's salt,* from the alchemist Glauber, who first used it as a medicine. Large quantities of a mixture of the anhydrous sulfate and carbon are used in making glass (Fig. 185, A).

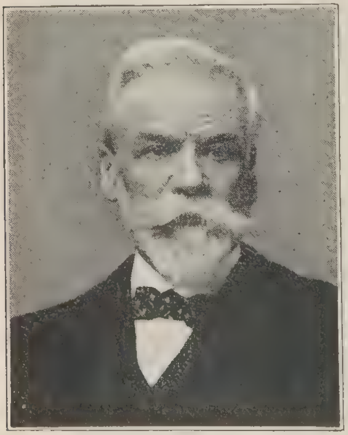


FIG. 250. Ernest Solvay (1835–1922)

A famous Belgian manufacturing chemist who developed the Solvay process for making sodium carbonate

545. The carbonates of sodium. Carbonic acid (§ 245), being a dibasic acid, forms two sodium salts: the normal carbonate, Na_2CO_3, and the acid carbonate, $NaHCO_3$. Both of these salts are white solids and both of them are well known in our homes, the former under the name of *sal soda* or *washing soda,* and the latter as *baking soda.*

546. Sodium carbonate (soda) (Na_2CO_3). This compound is also called soda ash and washing soda. Small percentages of the sodium salts of organic acids occur in many plants, especially in those that grow in sea water. When these plants are burned, the sodium compounds present are changed into sodium carbonate, which remains in the ashes. In former times sodium carbonate was obtained entirely from seaweeds by this method; hence the name *soda ash*. During the French Revolution the supply was cut off from France, and the French chemist Leblanc devised a method for making it from sodium chloride, of which France had large supplies. Leblanc's method proved much superior to the old method and was used exclusively for many years. It is still used to some extent in Europe, but in the United States it has given way entirely to the process devised by Solvay, a Belgian (Fig. 250).

547. The Solvay process. In this process carbon dioxide and ammonia are passed into a saturated solution of sodium chloride. These compounds react to form the acid carbonate, $NaHCO_3$:

$$NH_3 + CO_2 + NaCl + H_2O \longrightarrow NaHCO_3 + NH_4Cl \quad (1)$$

The acid carbonate formed is not very soluble, so that it separates. It is then filtered off and converted into the carbonate by heating:

$$2\,NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2 \quad (2)$$

The ammonium chloride (NH_4Cl) in equation (1) is used in preparing more ammonia; likewise the carbon dioxide liberated in equation (2) is used for making more of the acid carbonate according to equation (1). After the process is under way, the only additional compounds required to carry it on are water, sodium chloride, and some calcium hydroxide for liberating the ammonia from the ammonium chloride (Fig. 134). This is a very ingenious process, for the by-products formed are used in preparing the main product.

When sodium carbonate is crystallized from water it forms large crystals of the formula $Na_2CO_3 \cdot 10\,H_2O$, and it is this hydrate that is usually known as *washing soda* or *sal soda*. Its solution in water has a mild alkaline reaction and is used for laundry purposes. Mere mention of the fact that it is used in the manufacture of glass, soap, and many chemical reagents will indicate its importance in the industries. It is one of the few soluble carbonates.

548. Sodium acid carbonate ($NaHCO_3$). This compound is known also as sodium hydrogen carbonate, sodium bicarbonate, and baking soda. It is a constituent of all baking powders, and is used in our homes in the making of such foods as biscuits and cakes. It is prepared in the Solvay process as explained above, and it can also be made by passing carbon dioxide into a saturated solution of the normal carbonate:

$$Na_2CO_3 + H_2O + CO_2 \longrightarrow 2\ NaHCO_3$$

549. Sodium nitrate ($NaNO_3$). This substance, known also as Chile saltpeter, or simply "nitrate," is found in nature in certain desert regions where apparently it has been formed by the decay of organic substances in the presence of air and sodium salts. The largest deposits are in Chile (Fig. 251), and most of the nitrate of commerce comes from that country. Smaller deposits occur in California and Nevada. The commercial salt is prepared by dissolving the crude nitrate (known as *caliche*) in water, allowing the insoluble earthy materials to settle, and evaporating to crystallization the clear solution so obtained. The soluble impurities remain for the most part in the mother liquors.

Since this salt is the only nitrate found extensively in nature, it is the source from which other nitrates, including nitric acid, are prepared. Enormous quantities are used as a fertilizer, though air nitrates (§ 294) make it less important than formerly.

550. Other compounds of sodium. Among the other important compounds of sodium the following may be mentioned: (1) *Sodium thiosulfate* ($Na_2S_2O_3 \cdot 5\ H_2O$), commonly known as *sodium hyposulfite* or, in photography, simply *hypo*. It is used in photography to dissolve from the plate or film those silver salts that have not been acted upon by the light. (2) *Sodium cyanide* (NaCN) is used in preparing prussic acid (§ 306) and in the extraction of gold from its ores. (3) *Sodium iodide* (NaI) and *sodium bromide* (NaBr) are used in medicine and photography.

FIG. 251. Deposit of sodium nitrate in Chile

551. Hydrolysis of salts. In connection with neutralization (§ 237) we learned that when an acid and a base are brought together in solution the hydroxyl ion of the base and the hydrogen ion of the acid unite to form water, leaving the ions of the salt, which form a neutral solution. From this it might be inferred that solutions of all salts in water are neutral to indicators. This is true *if both acid and base from which the salt is formed are strong ones*. If either is very weak, then the water acts upon the salt and to a slight extent reverses the action of neutralization. Thus in the case of sodium carbonate we have a slight reaction, which quickly reaches equilibrium, as follows:

$$Na_2CO_3 + H_2O \rightleftarrows NaOH + NaHCO_3$$

The action of water on a salt to form an acid and a base is called hydrolysis. Since the hydrogen of the $NaHCO_3$ is a part of the *weak acid* H_2CO_3, it is little ionized, while the NaOH formed is a *strong base* and is very largely ionized. Consequently the resulting solution is *alkaline in reaction.* For the same reason soap is alkaline toward litmus (§ 516). In general, the water solutions of *all sodium and potassium salts of weak acids are alkaline in reaction.* For a similar reason the water solutions of *all salts of a weak base with a strong acid are acid in reaction.* For example,

$$CuSO_4 + 2\,H_2O \rightleftarrows \underset{\text{weak base}}{Cu(OH)_2} + \underset{\text{strong acid}}{H_2SO_4}$$

Compounds of Potassium

552. Occurrence. By reference to § 23 it will be seen that sodium and potassium are about equally abundant in the earth's crust. Potassium is a constituent of many igneous rocks, such as the feldspars and micas. Very large deposits of the chloride and the sulfate, along with compounds of calcium and magnesium, are found at Stassfurt, Germany (*Stassfurt salts*). Similar deposits occur in Alsace, France.

The natural decomposition of rocks containing potassium gives rise to various compounds of the element in all fertile soils. Its soluble compounds are absorbed by growing plants and built up into complex vegetable tissues; when these are burned, the potassium remains in the ash in the form of carbonate. The crude carbonate can be separated from wood ashes by dissolving it in water. This was formerly the chief source of potassium compounds, but they are now prepared from salt deposits, chiefly those of Germany and France.

The salt deposits consist of definite minerals (Fig. 252), the most important of which, besides salt, are the following:

Sylvite	KCl
Carnallite	$KCl \cdot MgCl_2 \cdot 6\,H_2O$
Kainite	$KCl \cdot MgSO_4 \cdot 3\,H_2O$
Kieserite	$MgSO_4 \cdot H_2O$

553. Properties. The compounds of potassium are so similar in properties to the corresponding compounds of sodium that for many uses (other than as fertilizers or as remedies in medical practice) they can be interchanged. The compounds of potassium, being as a rule more expensive, are not so widely used as those of sodium. The methods of preparation are in general the same as those used in preparing the corresponding compounds of sodium.

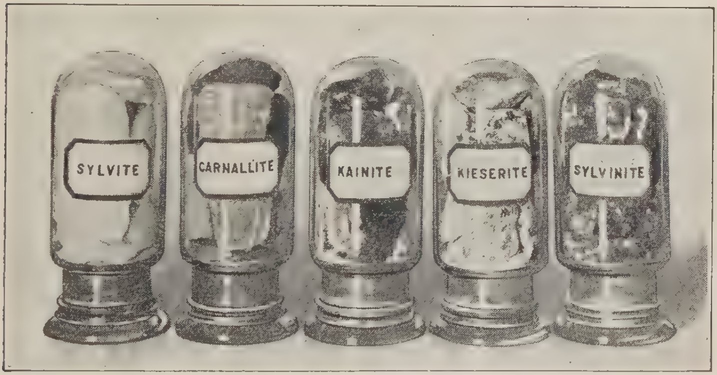


FIG. 252. The most important of the minerals constituting the Stassfurt salts

554. Potassium chlorate ($KClO_3$). It will be recalled that we prepared oxygen in the laboratory by heating potassium chlorate (§ 39, 3). This is the potassium salt of chloric acid ($HClO_3$). It is made by the action of chlorine on hot solutions of potassium hydroxide. The reaction is somewhat complex, as is shown by the following equation:

$$3\,Cl_2 + 6\,KOH \longrightarrow 5\,KCl + KClO_3 + 3\,H_2O$$

It is a white crystalline substance, and is used chiefly as an oxidizing agent in the manufacture of matches, fireworks, and explosives; it is also used in the laboratory preparation of oxygen and in medicine.

555. Potassium nitrate (saltpeter) (KNO_3). This salt is found in some regions where the climate is hot and dry, being formed by the decay of nitrogenous organic matter in the presence of earthy material containing compounds of potassium. The saltpeter used in making gunpowder was formerly made by imitating these conditions. At present it is prepared by the action of sodium nitrate upon potassium chloride (the former compound being obtained from Chile and the latter from Germany or France):

$$NaNO_3 + KCl \longrightarrow KNO_3 + NaCl$$

Potassium nitrate is a white solid. It is an excellent oxidizing agent. and is chiefly used in the manufacture of gunpowder. Smaller amounts are used in medicine and as a preservative for meats.

Since the compounds of sodium are as a general rule very similar to those of potassium, and, being cheaper, are more largely used, what is the reason for using potassium chlorate and potassium nitrate in place of the corresponding compounds of sodium? The reason is that sodium chlorate is difficult to prepare pure because it is very soluble, while sodium nitrate is deliquescent (§ 117) and therefore is not adapted for the manufacture of gunpowder, which must be kept dry.

556. Other compounds of potassium. *Potassium chloride* (KCl), *potassium bromide* (KBr), and *potassium iodide* (KI) are all white solids. The bromide and the iodide are both used in the preparation of photographic reagents and in medicine. *Potassium carbonate* (K_2CO_3), *potassium bicarbonate* ($KHCO_3$), *potassium sulfate* (K_2SO_4), and *potassium bisulfate* ($KHSO_4$) are all well-known compounds. They are white solids, readily soluble in water.

557. Sources of potassium salts in the United States. The great use of potassium salts is for fertilizer; the chloride and the sulfate are usually sold for this purpose.

Previous to the World War practically all our supply came from Germany. During the war and since that time an extended effort has been made to develop adequate sources of potassium compounds within our own borders. In this we have been only partially successful; however, an increasing amount of these salts is obtained from the deposits in Searles Lake, California (Fig. 253). Large deposits have been found recently in Texas which promise a future supply. By far the largest amount consumed in the United States still comes from Germany and France.

FIG. 253. Searles Lake, California

Searles Lake is a salt bed in the desert and for the most part contains no water

558. Gunpowder. Gunpowder is a mixture of potassium nitrate sulfur, and charcoal. When such a mixture is ignited, complicated reactions occur which result in the formation of a number of products, the chief of which are carbon dioxide, carbon monoxide, nitrogen, and the carbonate, sulfate, and sulfide of potassium. It is not nearly so powerful an explosive as nitrocellulose (§ 494) and nitroglycerin (§ 517), and it has largely been replaced by these.

Salts of Ammonium

559. Composition. When ammonium hydroxide (NH_4OH) is neutralized with acids, there are formed the corresponding salts, known as the *ammonium salts.* Since the ammonium radical is univalent, ammonium salts resemble those of the alkali metals in their formulas; they also resemble the latter salts very much in many chemical properties, and may be conveniently described in connection with them. Among the ammonium salts the chloride, sulfate, carbonate, and sulfide are the most familiar.

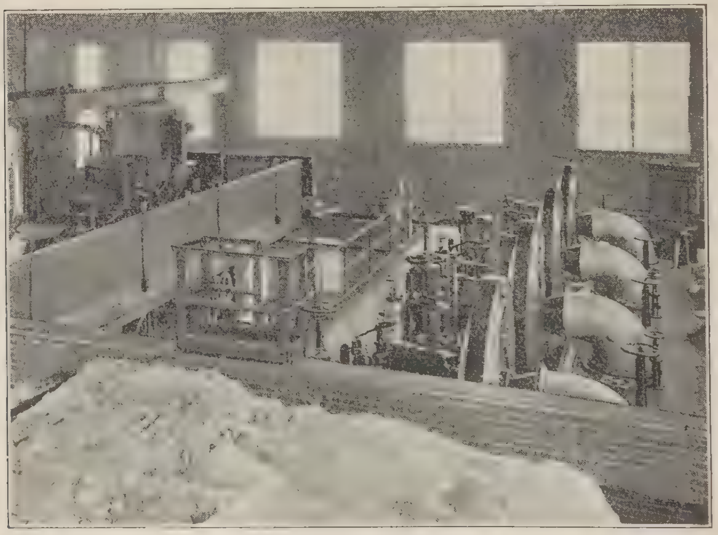


FIG. 254. Plant for the recovery of ammonium sulfate as a by-product in distilling coal (§ 464)

A large quantity of the recovered sulfate is shown in the foreground

560. Ammonium chloride (sal ammoniac) (NH_4Cl). This is a white solid. When heated it partly decomposes into ammonia and hydrogen chloride, which recombine as the temperature falls:

$$NH_4Cl \rightleftarrows NH_3 + HCl$$

This salt is used in soldering, since the hydrogen chloride evolved by the heat removes the oxide from the surface of the metals. It is also used in making dry cells, in medicine, and as a chemical reagent.

561. Ammonium sulfate ($(NH_4)_2SO_4$). This salt is prepared at low cost by passing ammonia into sulfuric acid. It is especially valuable as a fertilizer (Fig. 254), and large quantities are used for this purpose.

562. Carbonates of ammonium. Both the normal carbonate, $(NH_4)_2CO_3$, and the acid carbonate, NH_4HCO_3, are white solids, readily soluble in water. They are important chemical reagents.

563. Ammonium sulfides. Ammonium sulfide ($(NH_4)_2S$) and ammonium hydrogen sulfide (NH_4HS) are obtained when hydrogen sulfide and aqua ammonia are brought together in the proper proportions:

$$NH_4OH + H_2S \longrightarrow NH_4HS + H_2O$$
$$2\,NH_4OH + H_2S \longrightarrow (NH_4)_2S + 2\,H_2O$$

This solution is usually known simply as ammonium sulfide. It is used in chemical analysis as a reagent in testing for certain metals.

564. Flame reactions. A number of the metals, when heated in a colorless flame such as that of a Bunsen burner, give a characteristic color to the flame. Thus, sodium (or any of its compounds that will volatilize in the heat of the flame) makes the flame yellow; potassium and its compounds color the flame a pale violet; lithium colors it a deep crimson red.

Advantage is taken of these facts in testing for the presence of the elements in different substances. The test is best made by using a platinum wire, one end of which is fused into a piece of glass tubing that serves as a handle.

The other end of the wire is dipped into water and rubbed in the substance to be tested (or dipped into a concentrated solution of the substance), and the wire with the adhering particles is held in the outer edge of the base of the Bunsen flame (Fig. 255). The light from the sodium flame is absorbed in passing through blue glass, while that from potassium is not absorbed. Advantage is taken of this difference in detecting the two elements in mixtures.

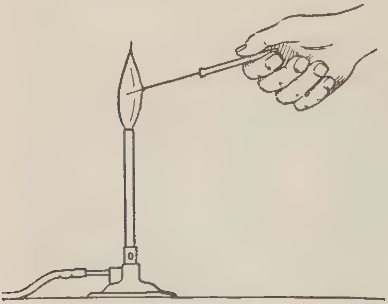


FIG. 255. Making a flame test

CHAPTER SUMMARY IN QUESTION FORM

1. (*a*) Can a metal be an alkali? (*b*) Why is the term *alkali metals* applied to the metals included in this chapter?

2. Which are the more important commercially, the alkali metals or their compounds?

3. Construct a table for five compounds of sodium, giving the following information:

CHEMICAL NAME	FORMULA	COMMON NAME (IF ANY)
1.		
2.		
3.		
4.		
5.		

4. State two ways by which sodium chloride is taken from the earth.

5. State how many sodium salts are known of each of the following acids: (*a*) carbonic acid; (*b*) nitric acid; (*c*) sulfuric acid; (*d*) phosphoric acid (§ 392).

6. Give the names and formulas of each of the salts referred to in the preceding question.

7. Is it reasonable to predict that each of the alkali metals will form the same number of salts as sodium, and similar in character?

8. Give the common names of each of the compounds represented by the following formulas, and give a reason why each name is appropriate: (*a*) $NaCl$; (*b*) $NaHCO_3$; (*c*) Na_2CO_3; (*d*) $Na_2SO_4 \cdot 10\,H_2O$; (*e*) $NaNO_3$.

9. Study the equations in § 547 for the preparation of sodium carbonate, and answer the following questions regarding them: (*a*) Why is salt used? (*b*) Why is carbon dioxide used? (*c*) What property has sodium bicarbonate that makes it possible to separate it? (*d*) What use is made of the by-product carbon dioxide? (*e*) How can we obtain ammonia from the by-product ammonium chloride, so as to use it again?

10. Rearrange the names of the compounds in column *A*, below, so that each one will stand opposite the most closely associated term in column *B*.

A	*B*
Sodium thiosulfate (hypo)	Fertilizers
Sal soda	Manufacture of glass
Soda ash	Laundry purposes
Caustic soda	Baking
Sodium nitrate	Soap
Sodium bicarbonate	Food condiment
Sodium chloride	Photography

11. Complete each of the following equations if hydrolysis occurs:

$$NaCl + H_2O \longrightarrow$$
$$Na_2CO_3 + H_2O \longrightarrow$$
$$CuSO_4 + 2\,H_2O \longrightarrow$$

12. (*a*) What is the great use of potassium compounds? (*b*) Where is the chief source of these compounds?

13. For what purpose is potassium nitrate better adapted than sodium nitrate?

14. State (*a*) one way in which the ammonium radical resembles the alkali metals; (*b*) one way in which the ammonium salts resemble the salts of the alkali metals.

15. State what ions are present in water solutions of each of the following compounds: (*a*) sodium hydroxide; (*b*) sodium carbonate; (*c*) sodium sulfate.

16. In the preceding question, what one ion is common to all the solutions?

THOUGHT QUESTIONS

1. (*a*) Write the formulas for each of the carbonates of sodium. (*b*) How could you prepare carbon dioxide from each of these? (*c*) If you had equal weights of each, which would give you the most carbon dioxide?

2. What are the products formed by passing a current of electricity through a water solution of (*a*) potassium chloride? (*b*) potassium sulfate?

3. Write the equation for the reaction that would enable you to change (*a*) sodium carbonate into sodium bicarbonate; (*b*) sodium bicarbonate into sodium carbonate.

4. In question 3, state the reason why each reaction completes itself.

5. In former times the farmers made much of their soap by boiling waste fats with the liquid obtained by pouring water on wood ashes. (*a*) Explain why soap can be made in this way. (*b*) Would the soap so formed be hard or soft (§ 514)?

6. Give the names of the substances already studied that are prepared from each of the following compounds: (*a*) ammonium chloride; (*b*) ammonium nitrate; (*c*) sodium nitrate; (*d*) potassium chlorate.

7. In the preparation of what compound already studied is sodium sulfate a by-product?

8. (*a*) Study the formula of borax (§ 422) and state whether this compound is an acid, a base, or a salt. (*b*) What effect do you think a water solution of borax would have on blue litmus and on red litmus?

9. A solution of sodium chloride has no effect on either blue or red litmus, while sodium carbonate turns red litmus blue. Explain.

10. 1 kg. of sal soda contains what weight of water of hydration?

11. Suppose that a soda-acid fire extinguisher (§ 170) is charged with 4000 g. of sodium bicarbonate and sufficient sulfuric acid to react with it completely. Calculate the volume of the carbon dioxide that would be evolved.

FOR HONOR STUDENTS

1. Read that part of Chapter III of "Creative Chemistry," entitled "Feeding the Soil," that tells the story of the use of potassium compounds and the sources of these compounds. Write a theme giving the interesting facts on this subject.

2. Suppose you had an abundant supply of sodium chloride. Tell how you could prepare each of the following substances from it, writing the equations for all the reactions involved: (*a*) sodium sulfate; (*b*) sodium carbonate; (*c*) sodium bicarbonate; (*d*) sodium hydroxide; (*e*) hydrochloric acid; (*f*) sodium; (*g*) chlorine; (*h*) potassium chlorate.

3. If a supply of wood ashes is available, repeatedly extract, say, 5 lb. of them with water, and see if you can make soap in the way the farmers formerly made it.

CHAPTER XXXVII

CALCIUM AND ITS RELATIVES

565. ***Introduction.*** In this chapter we shall discuss the metal calcium and its near relatives, strontium and barium. The metals themselves are light; only calcium has any commercial uses, and even these are very limited. The importance of these elements lies in their compounds, especially those of calcium. To appreciate this it is only necessary to mention such well-known substances as limestone, marble, lime, cement, plaster, mortar, window glass, and bones, all of which contain calcium compounds as an essential constituent. All three of the metals are bivalent in their compounds.

Calcium and its Compounds

566. The pure metal. Calcium is prepared just as we prepare sodium, namely, by the electrolysis of one of its melted compounds. Moreover, it resembles sodium in being very light (it is only one fifth as heavy as iron), and in decomposing water, forming calcium hydroxide and liberating hydrogen:

$$Ca + 2\,H_2O \longrightarrow Ca(OH)_2 + \overline{H_2}$$

The fact that it is acted upon so readily by both water and air restricts the use of the metal so that it has few commercial applications.

567. Calcium carbonate ($CaCO_3$). Enormous quantities of calcium carbonate occur in nature. *Limestone* is the most abundant form and sometimes constitutes whole mountain ranges. Limestone is never pure calcium carbonate, but contains variable percentages of magnesium carbonate, clay, silica, and compounds of iron. *Pearls, coral,* and various *shells* are largely calcium carbonate. *Calcite* is a very pure crystalline form and often is found in large transparent crystals (Fig. 256) called *Iceland spar. Marble* is composed of very small calcite crystals.

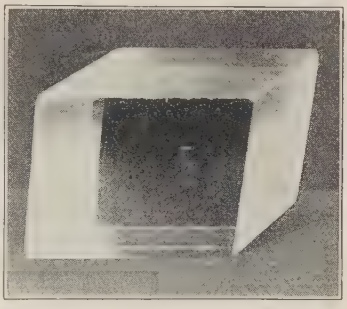


FIG. 256. A crystal of Iceland spar

In the laboratory pure calcium carbonate can be prepared by mixing solutions of a calcium salt and a soluble carbonate:

$$Na_2CO_3 + CaCl_2 \longrightarrow \underline{CaCO_3} + 2\ NaCl$$

When prepared in this way it is a soft white insoluble powder often called *precipitated chalk*, and is much used as a polishing powder (tooth powder).

The natural varieties of calcium carbonate find many uses, as in the preparation of lime and of carbon dioxide; in metallurgical operations, especially in making iron and steel; in the manufacture of soda and glass; for building-stone (Fig. 257); and as ballast for roads.

568. Calcium acid carbonate ($Ca(HCO_3)_2$). Carbonic acid has the formula H_2CO_3. Since calcium is bivalent, one calcium atom will displace both of the hydrogen atoms in the molecule of carbonic acid, thus forming the normal salt $CaCO_3$. How, then, is it possible to form a calcium *acid* carbonate? The answer is, by displacing one atom of hydrogen in each of two molecules of carbonic acid. The formula of this salt is $Ca\begin{smallmatrix}\diagup HCO_3\\ \diagdown HCO_3\end{smallmatrix}$ or, more briefly, $Ca(HCO_3)_2$.

The normal calcium carbonate is insoluble in pure water; however, *it readily dissolves in water containing carbonic* *acid.* This is due to the fact that the normal carbonate reacts with carbonic acid to form the acid salt, which is very soluble:

$$CaCO_3 + H_2CO_3 \rightleftarrows Ca(HCO_3)_2$$

The resulting acid carbonate exists only in solution. If we attempt to get it by evaporating the solution, it decomposes into carbonic acid and the normal carbonate, which, being insoluble, precipitates. The reaction represented by the above equation is therefore a reversible one, and will go in either direction, depending on conditions.

FIG. 257. The Lincoln Memorial at Washington, built of white marble and limestone

569. Formation of caves. Carbon dioxide often occurs in porous rocks and underground fissures. Natural waters coming in contact with this gas dissolve large percentages of it, forming carbonic acid (§ 168). From what we have learned in the previous paragraph, it is evident that such waters will readily dissolve limestone which is chiefly calcium carbonate. This solvent action, continued through the ages, has resulted in the formation of caves, some of them very large, as the Mammoth Cave of Kentucky. Water trickling through the roofs of these caves evaporates, depositing calcium carbonate, which, as the process continues, often forms icicle-shaped masses known as *stalactites*; or the waters may drip upon the floor of the cave and there form similar masses known as *stalagmites* (Fig. 258).

570. Calcium oxide (lime) (CaO). Almost everyone is familiar with *lime*, or *quicklime*, as we sometimes call it. We know that when water is added to it heat is evolved, and we say that the lime is *slaked*. It will be of interest to know just what lime is, how it is prepared, and what are the properties that make it such a valuable compound.

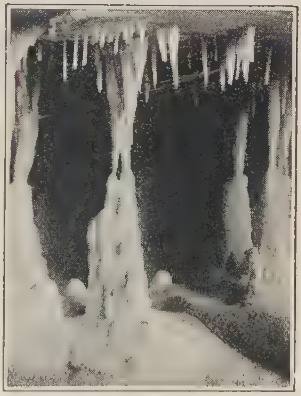


FIG. 258. Stalactites and stalagmites

Lime is impure calcium oxide. It is made by heating limestone in large kilns (limekilns) as explained in Fig. 259. If we heat pure calcium carbonate, we obtain pure calcium oxide:

$$CaCO_3 \longrightarrow CaO + CO_2$$

When we heat limestone the same reaction takes place, but the impurities in the limestone remain in the oxide.

Lime is a white substance that melts only in the intense heat of the electric furnace. Water reacts with it, forming calcium hydroxide, much heat being evolved in the process:

$$CaO + H_2O \longrightarrow Ca(OH)_2 + 15{,}540 \text{ cal.}$$

Because of its affinity for water, lime is used to dry gases. When exposed to the air it absorbs water and also carbon dioxide, being changed into a carbonate. It is then said to be *air-slaked.* Several million tons are produced annually in the United States, most of which is used in making calcium hydroxide.

571. Calcium hydroxide (slaked lime, hydrated lime) ($Ca(OH)_2$). This compound is prepared by adding water to lime, as explained above. When pure it is a light, white powder. It is sparingly soluble in water, forming a strongly alkaline solution called *limewater.* Owing to its cheapness it is used in the industries whenever an alkali is desired. It is used in the preparation of ammonia, bleaching powder, and the hydroxides of sodium and potassium. It is also used to remove sulfur compounds and carbon dioxide from

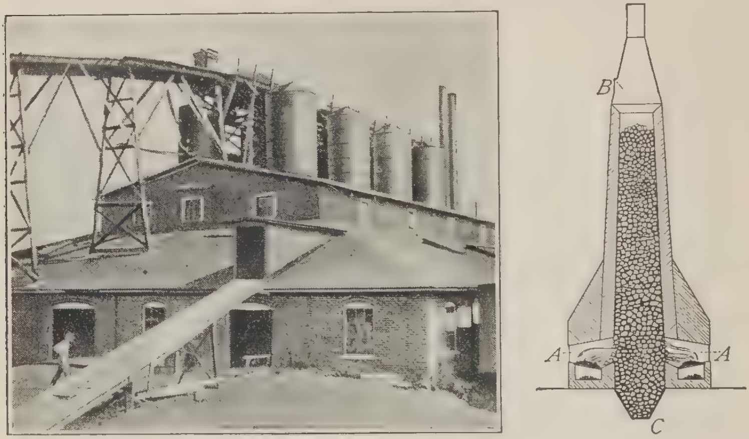


FIG. 259. A group of limekilns in a modern plant and a vertical section of one kiln

A modern limekiln is a group of units, one of which is represented in vertical section. Fire boxes, *A*, *A*, are built around the base of the kiln, all leading into the central stack. The kiln is filled with limestone through a door *B* from an elevated railroad. Hot products of combustion are drawn up through the kiln and the limestone is decomposed by their heat. Air is drawn in at *C*, and this cools the hot lime at the base of the kiln and at the same time furnishes hot oxygen for combustion. From time to time the lime is dropped into cars run under the kiln coal gas, to remove the hair from hides in making leather, for making mortar and plaster, and for neutralizing the acids in soils (§ 404).

572. Mortar and plaster. Mortar is made by mixing water, calcium hydroxide, and sand. When it is exposed to the air or spread upon porous materials, moisture is removed from it (partly by absorption into the porous materials and partly by evaporation) and the mortar becomes firm, or *sets*. At the same time carbon dioxide is slowly absorbed from the air and hard calcium carbonate is formed:

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

By this combined action the mortar becomes very hard and adheres firmly to the surface upon which it is spread. The sand serves to give body to the mortar and makes it porous. It also prevents too much shrinkage. Plaster for walls is a mixture of calcium hydroxide (or calcium sulfate) and hair or wood fiber, the latter serving to hold the mass together.

573. Bleaching powder. When chlorine is passed over calcium hydroxide there is formed a white solid compound having the formula $CaOCl_2$ and known as *bleaching powder*, *chloride of lime*, or simply *bleach*:

$$Ca(OH)_2 + Cl_2 \rightleftarrows CaOCl_2 + H_2O$$

When this compound is treated with an acid, chlorine is evolved:

$$CaOCl_2 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + Cl_2$$

When exposed to the air, bleaching powder is slowly acted upon by moisture and carbon dioxide, evolving hypochlorous acid (HClO), an unstable compound, which is a good disinfectant. Bleaching powder is prepared in large quantities (Fig. 260) and used both as a disinfectant and as a bleaching agent, although it is gradually being replaced by liquid chlorine (§ 215, 2).

574. Calcium sulfate ($CaSO_4$). Calcium sulfate occurs in nature in several different forms, the most common of which is *gypsum* ($CaSO_4 \cdot 2\ H_2O$). This is quarried in large amounts in New York, Iowa, and Michigan. It is used as a filler in making paper (§ 491), as a constituent of fertilizers, and especially in making *plaster of Paris.* It is but slightly soluble in water.

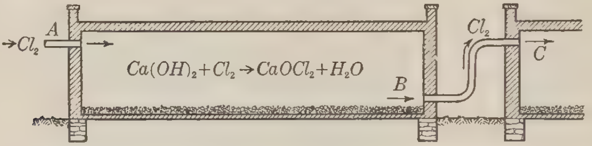


FIG. 260. Chambers for the manufacture of bleaching powder

Calcium hydroxide is spread to a depth of two or three inches upon the floor of a room, made of lead or concrete. The chlorine enters near the top at *A*. Any unabsorbed chlorine passes out at *B* and into the adjoining chamber at *C*. The commercial product ordinarily contains about 35 per cent of chlorine. It is shipped in sealed packages or iron drums

575. Plaster of Paris ($(CaSO_4)_2 \cdot H_2O$). This is a fine white powder obtained by carefully heating gypsum. When water is added to the powder a plastic mass is formed which quickly hardens, or *sets*. This property makes it valuable for molding casts, for stucco work, and for a finishing coat on plastered walls. Broken bones are often held in place by casts of plaster of Paris until they grow together.

576. Calcium carbide (CaC_2). The great value of calcium carbide lies in the fact that it gives us a cheap source of acetylene, and also of the important fertilizer known as *cyanamide.* The discovery of a simple way of making calcium carbide was the result of an accident. Willson, a Canadian engineer, was trying to prepare the metal calcium. To do this he heated a mixture of lime and coke in an electric furnace, hoping that the hot carbon (coke) would combine with the oxygen of the lime, and thus set free the calcium. To his disappointment he found that in place of

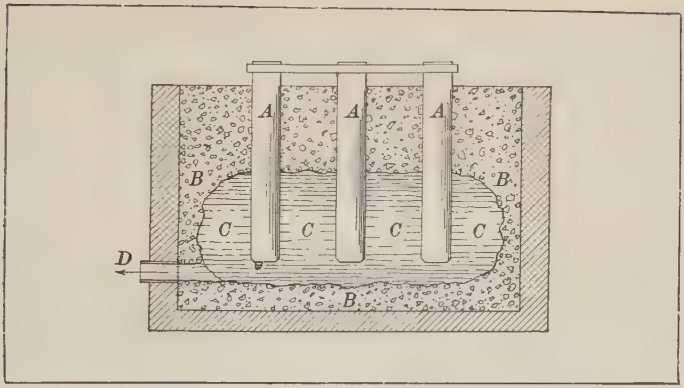


FIG. 261. A furnace for making calcium carbide

A large brick box open at the top is fitted with carbon electrodes *A*, *A*, *A*, and filled with a mixture, *B*, of lime and coke. Sufficient current is used to secure a temperature of about 2000°. The lime and coke react to form calcium carbide, *C*, which melts as fast as it forms and is drawn off from time to time at *D*

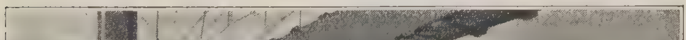


FIG. 262. View in a plant for making calcium carbide, showing the large carbon electrodes which dip into the furnace below

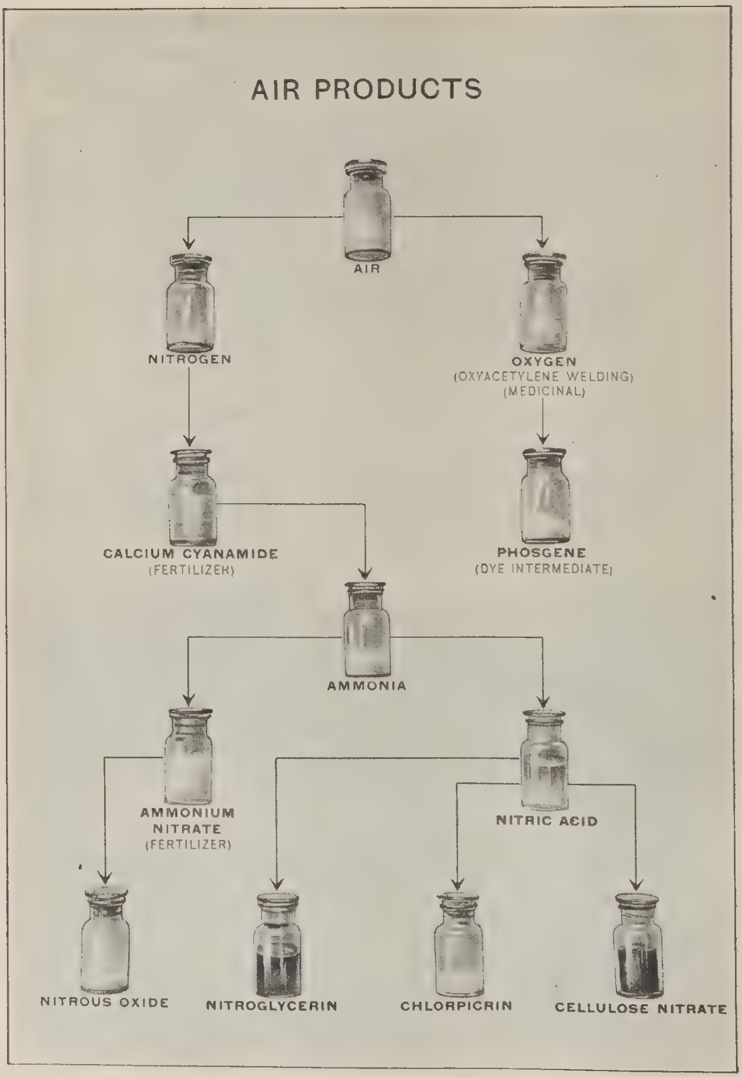

AIR PRODUCTS
AIR
NITROGEN
OXYGEN
(OXYACETYLENE WELDING)
(MEDICINAL)
CALCIUM CYANAMIDE
(FERTILIZER)
PHOSGENE
(DYE INTERMEDIATE)
AMMONIA
AMMONIUM NITRATE
(FERTILIZER)
NITRIC ACID
NITROUS OXIDE
NITROGLYCERIN
CHLORPICRIN
CELLULOSE NITRATE

FIG. 263. Some products obtained from the air

calcium he obtained a gray solid. He tossed this away, and some of it chanced to fall into a bucket of water; Willson was surprised to see that bubbles of gas were evolved. He soon found that the solid he had obtained was *calcium carbide*, and that water reacts with this to form acetylene. The discovery which he made has turned out to be of far greater importance than the one he earnestly hoped to make.

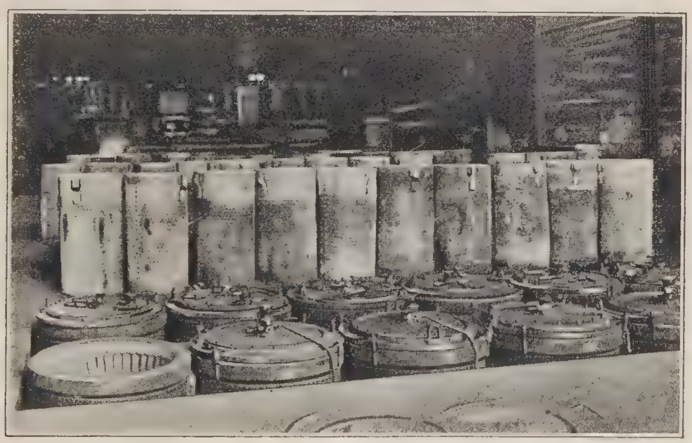


FIG. 264. View in a plant for making calcium cyanamide

Calcium carbide is placed in the perforated steel cans shown in the background. These are then lowered into the furnaces shown in the foreground. The carbide is heated to about 1000°, and then pure nitrogen obtained from liquid air is passed over it, the two combining to form the cyanamide

Calcium carbide is now made on a large scale by heating a mixture of coke and lime in an electric furnace (Figs. 261, 262), just as Willson first made it:

$$CaO + 3\ C \longrightarrow CaC_2 + CO$$

577. Calcium cyanamide ($CaCN_2$). When nitrogen is passed over hot calcium carbide the two react, forming a compound known as *calcium cyanamide* (Fig. 264):

$$CaC_2 + N_2 \longrightarrow CaCN_2 + C$$

The commercial product is impure, containing about 60 per cent of the calcium cyanamide; the impurities are lime and carbon. This is ground, moistened with water (to slake the lime present), and in dry form sold as a fertilizer under the name of *cyanamide*. Its value as a fertilizer lies in the fact that all its nitrogen is available as a plant food.

Calcium cyanamide is also used as a source of ammonia as well as of sodium cyanide, thus:

$$CaCN_2 + 3\ H_2O\ \text{(steam)} \longrightarrow CaCO_3 + 2\ NH_3$$
$$CaCN_2 + C + 2\ NaCl \longrightarrow CaCl_2 + 2\ NaCN$$

578. Calcium chloride ($CaCl_2$). This compound occurs in some natural waters, and is also a by-product in the Solvay process (§ 547). It attracts moisture from the air (is deliquescent), and because of this property it is being used to lay the dust on roads and tennis courts.

579. Calcium phosphate ($Ca_3(PO_4)_2$). Attention has already been called to this compound and to its value as a fertilizer (§ 407, 2). It is the chief mineral constituent of bones; hence *bone ash* is largely calcium phosphate.

580. Nitrogen fixation. Formerly the sodium nitrate deposits of Chile were the sole source of all the nitric acid of commerce and of most of the nitrates used as fertilizers, while our supply of ammonia came entirely from the destructive distillation of coal. In recent years methods have been devised for preparing these compounds from the nitrogen of the air. These processes are known under the general term of "nitrogen fixation." Of these, the Haber process (§ 283, 2, (a)) is the most important, followed by the cyanamide process referred to above. More than half of the world's supply of ammonia, nitric acid, and its salts is now prepared from atmospheric nitrogen, and the amounts so prepared are constantly increasing (Fig. 263).

Strontium and Barium

581. Strontium and barium. These two metals resemble calcium closely, but are much rarer and more difficult to prepare. Their volatile compounds when heated in a flame give a color to the flame, strontium coloring it red, and barium green; hence they are sometimes used in fireworks. Two compounds of barium are of importance: barium chloride ($BaCl_2 \cdot 2\ H_2O$) and barium sulfate ($BaSO_4$). The former is used in the laboratory as a reagent for the detection of sulfuric acid and soluble sulfates (§ 349); the latter is an insoluble white solid found in nature as the mineral *barite* or *heavy spar*, and used in the manufacture of white paints.

CHAPTER SUMMARY IN QUESTION FORM

1. State four ways in which calcium resembles sodium.

2. What are the properties of calcium that limit its use as a metal?

3. (*a*) What is the most abundant compound of calcium found in nature? (*b*) Write the names of six natural products (minerals or products of animals) that are composed entirely or largely of this compound. (*c*) Which of these six are the purest form of the compound?

4. Suppose you wish to prepare some pure calcium carbonate. (*a*) What compounds would you use in its preparation? (*b*) Write the equation for the reaction that takes place in its preparation. (*c*) State why the reaction goes to completion.

5. Write the formula (*a*) of the normal calcium carbonate; (*b*) of the acid calcium carbonate.

6. Contrast (*a*) the stability, and (*b*) the solubility in water, of the two carbonates referred to in question 5.

7. In § 539 you will find the statement that all normal carbonates except those of ammonium, sodium, and potassium are insoluble in water. (*a*) How do you explain the fact that the normal calcium carbonate *does* dissolve in ordinary soil waters? (*b*) Write the equation for any reaction that may take place in the process.

8. Write the equation for the reaction that takes place (*a*) in the formation of caves; (*b*) in the formation of stalactites and stalagmites.

9. Prepare a table which gives the following information in regard to five important compounds of calcium:

CHEMICAL NAME	COMMON NAME, IF ANY	FORMULA	ONE USE	PREPARATION OR SOURCE
1.				
2.				
3.				
4.				
5.				

10. Give the name and formula for (*a*) a calcium compound used to lay dust on roads; (*b*) one used as a fertilizer; (*c*) one discovered by chance.

11. (*a*) Explain what is meant by the phrase "fixation of nitrogen." (*b*) Give two important methods by means of which nitrogen is "fixed."

12. Barium sulfate is insoluble; what use is made of this property (*a*) in the laboratory? (*b*) in industry?

13. Oxidizable substances and nitrates are used in the manufacture of red and green lights. (*a*) What nitrates are used for this purpose? (*b*) Why not use sodium nitrate?

THOUGHT QUESTIONS

1. Some samples of Iceland spar and gypsum look very much alike. How could you distinguish between them?

2. Beads made of celluloid (§ 494) are often dyed and sold as coral beads. Suggest a way for detecting the fraud.

3. (*a*) What is the difference in composition between water-slaked lime and air-slaked lime? (*b*) Since the two products look alike, how could you distinguish between them?

4. Is the following reaction reversible, and if so, how can you make it go in either direction?

$$CaCO_3 \longrightarrow CaO + CO_2$$

5. If you blow exhaled air through limewater, a white precipitate forms, but this precipitate disappears if you continue to blow air through the liquid. If the resulting clear liquid is boiled, the white precipitate again forms. Account (giving equations for reactions involved) for (*a*) the formation of the precipitate, (*b*) its disappearance, and (*c*) its reappearance on boiling.

6. A town was using 2500 lb. of bleaching powder (35 per cent chlorine) daily for purifying its water supply. It was decided to replace the bleaching powder with liquid chlorine. How many pounds of chlorine would be required daily?

7. How many pounds of salt would be required to supply the amount of chlorine referred to in question 6?

8. Calculate the weight of water that would be required to slake 1 kg. of lime.

9. A plant for the production of lime has an output of 30 tons of lime a day. Assuming the limestone to be pure calcium carbonate, what weight of limestone would the plant require daily?

10. (*a*) One ton of calcium carbide will "fix" how many pounds of nitrogen? (*b*) If the resulting compound is acted upon by steam, how many pounds of ammonia will be formed?

FOR HONOR STUDENTS

1. Suppose you owned large quarries of limestone and wished to utilize this mineral in the manufacture of the products listed below. Write the equations for the reactions that would be involved in the preparation of each of these products from the limestone: (*a*) lime; (*b*) hydrated lime; (*c*) mortar; (*d*) bleaching powder; (*e*) calcium carbide; (*f*) cyanamide; (*g*) ammonia; (*h*) nitric acid (§ 294).

2. Collect and exhibit to the class as many minerals (or other products) as possible that contain calcium.

CHAPTER XXXVIII

MAGNESIUM, ZINC, AND CADMIUM

582. *Introduction.* These three metals form a typical family in the periodic table and resemble each other in the ways we should expect. Magnesium is only about one fourth as heavy as zinc, although it has a higher melting point. Cadmium is of relatively little importance, although it is sometimes used in alloys. All three metals are bivalent, so the formulas of their compounds are similar to the corresponding ones of calcium.

Magnesium

583. The element. Magnesium is one of the abundant elements, although it never occurs native. Like sodium and calcium, it is obtained by the electrolysis of its melted compounds; the mineral *carnallite* (§ 552) is used for this purpose. The pure metal is silver-white, and so light that it just fails to float on water. Air tarnishes it somewhat, and common acids readily dissolve it. When it is ignited it burns with great brilliancy in air, and gives a light rich in the rays which act upon photographic plates; hence its use for making photographic flash lights and fireworks and for the flares used in making signals at night (Fig. 265). Ordinary flash-light powder is a mixture of powdered magnesium and potassium chlorate or some similar oxidizing agent. Magnesium is also used in making alloys, such as *magnalium*, a light alloy of magnesium and aluminum sometimes used in the construction of airships.

584. Magnesium carbonate ($MgCO_3$). The pure carbonate occurs in nature as the mineral *magnesite.* More often it is associated with calcium carbonate to form *dolomite* ($CaCO_3 \cdot MgCO_3$), which forms whole mountain ranges and thick strata in the earth's crust. Like calcium carbonate, which it closely resembles, magnesium carbonate dissolves in water which contains carbonic acid, and forms the acid salt. When heated it decomposes into carbon dioxide and magnesium oxide (MgO). The latter resembles lime, and combines with water to form the hydroxide $Mg(OH)_2$. The oxide melts only at a very high temperature, and for this reason is used as a lining for furnaces.

FIG. 265. Illumination by a magnesium flare dropped from an airplane

Photograph by United States Army Air Corps

585. Magnesium sulfate ($MgSO_4$). Magnesium sulfate differs from calcium sulfate in that it is very soluble in water. From water it crystallizes as the hydrate $MgSO_4 \cdot 7\ H_2O$, which is used in medicine under the name of *Epsom salts.* It occurs in some mineral waters such as the famous spring in Epsom, England, from which the hydrate derives its common name. Large deposits of the nearly pure salt are found in Wyoming and Washington. It has many uses, especially in the dye industry.

586. Magnesium silicates. A number of important silicates are found in nature, including *talc,* also known as *soapstone,* and *asbestos.* Asbestos is mined in large quantities in the province of Quebec, Canada (Fig. 266), and is used in making a great variety of fireproof articles such as boards, shingles, and cloth; as a covering for hot-water and steam pipes to prevent loss of heat; and as an electrical insulator. Talc (soapstone) is used for making sinks and table tops, and, when finely ground, for toilet purposes.

FIG. 266. Mining asbestos in Quebec, Canada

587. Boiler scale. When hard water is used in steam boilers, there is often deposited in the pipes a hard layer of mineral matter known as *boiler scale* (Fig. 267). The formation of this scale is due to several causes, the chief ones being the following: (1) Calcium sulfate is almost insoluble in superheated water; if present in the water, it will be precipitated and form a scale. (2) The acid carbonates of calcium and magnesium, present in almost all waters, are decomposed by the heat (§ 568) and the normal insoluble carbonates formed are deposited. (3) Some magnesium salts undergo hydrolysis (§ 551), forming insoluble magnesium hydroxide.

Boiler scale causes much waste of heat. There are many preparations on the market which claim to prevent its formation, but the only sure way of doing this is to use soft water.

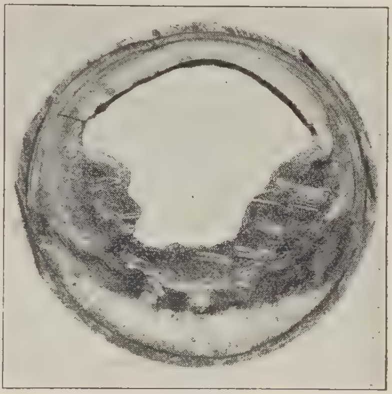


FIG. 267. Deposit of boiler scale inside a water tube of a boiler

Zinc

588. Historical. All the metals that we have so far studied are rather difficult to prepare, so that they were not obtained until comparatively recent times and they have not come into any extensive use. Zinc, on the other hand, is rather easily separated from its ores, and has long been known and used. Jewelry containing zinc has been found in the ruins of cities that were destroyed before the beginning of the Christian Era, but it was many centuries later that it was recognized as a metal distinct from lead or tin.

589. Properties. Zinc is the first of the metals so far studied that is familiar to all of us. It is a bluish-white metal, about as heavy as iron. If heated strongly in the air it takes fire and burns to the oxide, ZnO. If the metal is melted and allowed to cool, it crystallizes and at ordinary temperature is quite hard and brittle; but if heated to between 100° and 150° it becomes malleable and can be rolled into thin sheets, and in this form the metal retains its softness and malleability at ordinary temperatures. When melted and poured into water it forms thin, brittle flakes known as *granulated* or *mossy* zinc; this is the form used in preparing hydrogen. Air tarnishes it but exerts no further action. It dissolves in all the common acids.

590. Occurrence and metallurgy. Zinc does not occur free in nature, neither is it a constituent of common rocks. Its chief ores are the following: *sphalerite* (ZnS), *zincite* (ZnO), *smithsonite* ($ZnCO_3$), and *franklinite* ($ZnO \cdot Fe_2O_3$). The chief zinc-producing states are Oklahoma, Kansas, and New Jersey (Fig. 268).

When zincite is used as the source of zinc, it is only necessary to heat the ore with carbon to separate the metal. Other ores, when used, are first roasted in a current of air to convert them into the oxide (§ 534), which is then reduced with carbon. Thus the reactions that take place in the separation of zinc from sphalerite are represented by the equations

$$2\,ZnS + 3\,O_2 \longrightarrow 2\,ZnO + 2\,SO_2$$
$$ZnO + C \longrightarrow Zn + CO$$

591. Uses of zinc. The chief use of zinc is in the manufacture of *galvanized iron*. This consists of *sheets of iron covered with a thin layer of zinc, which protects the iron from rusting*. About two thirds of all the zinc produced is used in this way (Figs. 270, 271). Sheet zinc is used as a lining for sinks and water-containers. Large quantities of the metal are used in making brass and other alloys (§ 532), in the construction of electrical batteries, and in separating silver from lead. In the laboratory it is used in the preparation of hydrogen and, in the form of zinc dust, as a reducing agent.

592. The compounds of zinc. In general the compounds of zinc resemble the corresponding ones of magnesium in formula and appearance, although they differ greatly in chemical conduct. The two most widely used compounds are the oxide (ZnO) and the sulfide (ZnS).

593. Zinc oxide (ZnO). This oxide occurs in an impure state in nature. Commercially it is generally made by burning the metal in air. It is a pure-white powder which,

FIG. 268. Mining zinc and lead in Oklahoma

FIG. 269. Spraying a house with white paint containing zinc oxide and lithopone

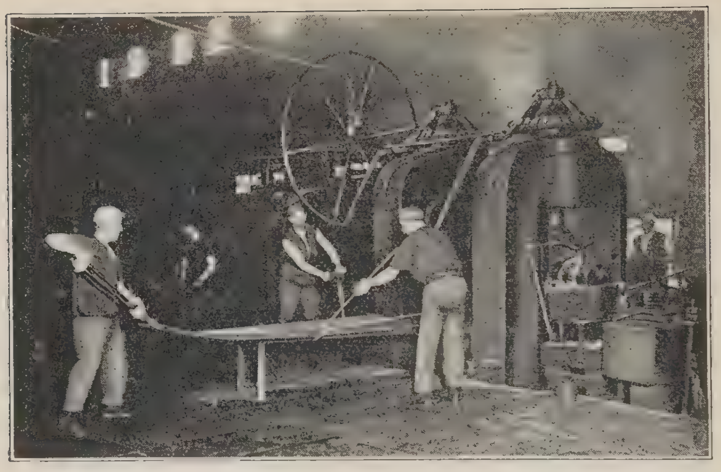


FIG. 270. Rolling sheet iron preparatory to galvanizing it with zinc

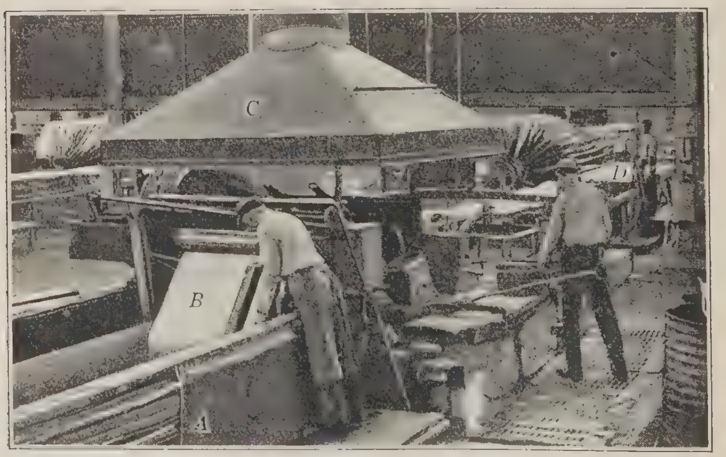


FIG. 271. Galvanizing sheet iron

The sheets of iron *B* are first cleaned by passing them through a vat *A* of dilute acid. They are then passed through a kettle of molten zinc, placed under the hood *C*, which carries away the poisonous fumes. The sheets are then passed between rollers, thus forming the finished product *D* under the name of *zinc white*, is much used as a white pigment in paints (Fig. 269). It has an advantage over white lead in that *it is not changed in color by sulfur compounds* (which are likely to be present in the air of manufacturing districts), while lead compounds turn black. Many thousand tons of zinc oxide are used in paints each year. It is also used as a filler in the manufacture of rubber goods, especially automobile tires.

594. Zinc sulfide (ZnS). Very large deposits of zinc sulfide occur in Missouri and Oklahoma, constituting the mineral *sphalerite*. *It is insoluble in water and, when pure, is white.* The very valuable white-paint pigment known as *lithopone* is a mixture of barium sulfate and zinc sulfide, made by bringing together barium sulfide and zinc sulfate in solution:

$$BaS + ZnSO_4 \longrightarrow \underline{BaSO_4} + \underline{ZnS}$$

595. Other compounds of zinc. Among the other compounds of zinc may be mentioned the sulfate, which crystallizes from water in the form of the hydrate, $ZnSO_4 \cdot 7\,H_2O$. This is commonly known as *white vitriol*, and is used in medicine and in the dyeing of cloth. The *chloride*, $ZnCl_2$, is used to preserve wood that must be partly buried in the ground, such as posts and railroad ties. Some coal-tar compounds are also used for the same purpose.

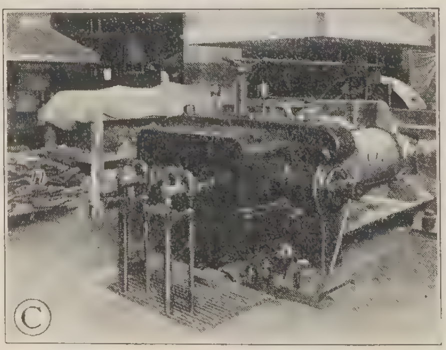
Rubber

596. Production. The statement has been made (§§ 162, 593) that carbon black and zinc oxide are largely used in making certain rubber goods, and this suggests a brief description of rubber itself and its application in the making of some important rubber article, such as the casing of an automobile tire.

Rubber is the product of various trees. The most important grows wild in the upper Amazon region and is cultivated in large numbers in tropical regions such as Java,

The rubber is obtained from rubber trees by tapping. The rubber, in the form of an emulsion, flows from the trees and is collected in cups and buckets, as shown in A. This emulsion resembles milk in appearance and is known as the *latex*

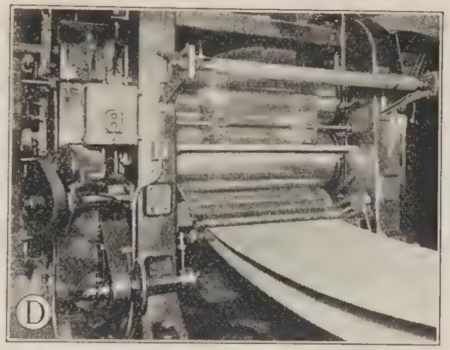
The rubber is obtained from the emulsion by coagulating it with acetic acid; or in a more primitive way by pouring the emulsion, a little at a time, over the end of a stick and evaporating the water over a fire, as shown in B



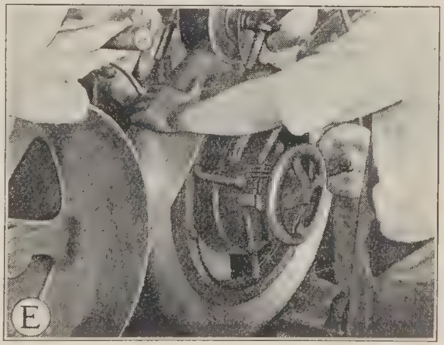
The raw rubber is next mixed (or compounded) with sulfur and certain substances such as zinc oxide and carbon black. This is done by running the materials between large revolving cylinders (*O*), as shown in C, until thoroughly mixed. Piles of the raw rubber are shown, marked *n*

FIG. 272, A, B, C. Some steps in the manufacture of automobile casings

In D cotton fabric is being impregnated with the compounded rubber by running the fabric and the rubber between large cylinders of metal. In cord tires the cord is wrapped about the core, and the cord as well as the interstices is filled with rubber



The method of building up the casing varies with the size and kind of tire desired. One method consists in winding the rubberized fabric on an iron wheel, the surface of which is the shape of the inner surface of the desired casing. Another method consists in building the casing flat by winding it on a flat drum, then forcing it into the desired shape



The tire casing is then placed in a mold as shown in F, and heated in large steam ovens. In this process the rubber is vulcanized and toughened. It is then removed and the finishing touches given it

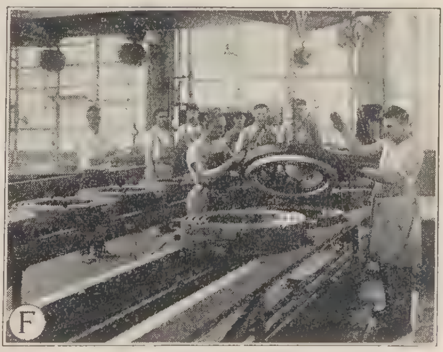


FIG. 272, D, E, F. Some steps in the manufacture of automobile casings

Sumatra, Ceylon, and the Malay States. The percentage of rubber obtained from the cultivated trees has increased very rapidly as the demand for rubber increased, until at the present time by far the largest amount comes from the rubber plantations. The rubber is obtained from the trees by tapping (cutting nearly through the bark). The sap runs from the cuts and is collected in cups, as shown in Fig. 272, A. This sap, which is known as the *latex*, is really an emulsion consisting mainly of minute rubber particles dispersed in water. It resembles milk in appearance, and is similar to milk in that the rubber particles are dispersed in it much as the fat is dispersed in milk. The rubber is separated by adding a little acetic acid, which causes the rubber to coagulate. An older method, still in limited use, consists in removing the water by evaporation, leaving the rubber. To do this, the latex is poured over the end of a stick, which is then revolved over the hot smoke from a fire (Fig. 272, B). When the water evaporates the process is repeated until finally a ball of rubber is built up.

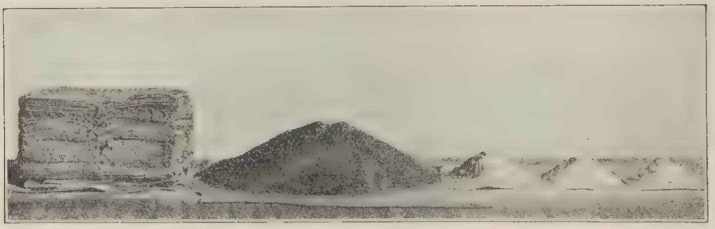


FIG. 273. Weighed-out materials for rubber mixture

The piles in order are rubber, carbon black, zinc oxide, and accelerators

597. Composition. Pure rubber is a hydrocarbon whose molecular formula is a multiple of the simple formula C_5H_8. It can be made in the laboratory, but the rubber made in this way costs much more than the natural product and hence cannot compete with it.

598. Vulcanizing rubber. The natural rubber is sticky and easily affected by the temperature, and as a result is worthless for most purposes. In 1839 Goodyear found that if the rubber is heated with sulfur these objectionable qualities are overcome. This process is known as *vulcanization.*

599. Compounding rubber. For most purposes the pure rubber is mixed or compounded with other materials, technically known as *fillers.* These fillers impart strength as well as other desired properties to the finished product. Carbon black and zinc oxide are the most common of these fillers (Fig. 273). There is also added a small amount of certain organic compounds known as *accelerators,* which shorten the time of vulcanization and add desirable qualities.

CHAPTER SUMMARY IN QUESTION FORM

1. When writing the formulas of the compounds of magnesium, zinc, and cadmium, of what advantage is it to know that these three elements belong to the same family?

2. Give two reasons for the use of magnesium in flash-light powders.

3. Give the name of the mineral composed (*a*) of pure magnesium carbonate; (*b*) of magnesium carbonate combined with calcium carbonate.

4. Write the names and formulas for four important compounds of magnesium.

5. Write the equations for the action (*a*) of heat on calcium carbonate and magnesium carbonate; (*b*) of water on calcium oxide and magnesium oxide; (*c*) of hydrochloric acid on calcium carbonate and magnesium carbonate. (*d*) Point out the similarity between the compounds of calcium and magnesium as shown in the above equations.

6. (*a*) Mention four compounds which are likely to be present in boiler scale, and (*b*) state the property of each that causes it to be deposited in the boiler pipes.

7. What is the reason that zinc is more familiar to you and has been longer known to mankind than any other metal so far studied?

8. What property has zinc that makes it useful (*a*) in the preparation of hydrogen? (*b*) in the manufacture of galvanized iron?

9. Why is zinc heated to between 100° and 150° more useful than zinc cooled rapidly from the melted state?

10. Write the equations for the reactions involved in the separation of zinc (*a*) from zincite; (*b*) from sphalerite.

11. Give in tabular form the following information with respect to two of the most largely used compounds of zinc: (*a*) chemical name; (*b*) common name; (*c*) formula; (*d*) source; (*e*) industry using it.

12. Lithopone is a mixture of what two compounds?

13. Describe the following in regard to rubber: (*a*) its source; (*b*) the separation of pure rubber; (*c*) its composition.

14. (*a*) Why is it necessary to heat rubber with sulfur before it is used? (*b*) What is the process called?

15. (*a*) Name the different substances used in making an ordinary tire casing, and (*b*) state the purpose of each.

THOUGHT QUESTIONS

1. (*a*) Select from the electrochemical series (§ 256) one univalent metal, one bivalent metal, and one trivalent metal that will replace hydrogen from acids. (*b*) Write the equation for the reaction of each of these metals with hydrochloric acid.

2. Write an equation showing how magnesium chloride, by hydrolysis, can form magnesium hydroxide.

3. Magnesium carbonate is a common medicine. One of the ingredients of the gastric juice in the stomach is hydrochloric acid. What reaction, if any, would take place between the magnesium carbonate and hydrochloric acid?

4. The preceding chapter stated that large caves are often formed in limestone rocks. Discuss the possibility of having such caves formed in magnesite rocks.

5. Suppose you had a supply of zinc and wished to prepare the following compounds. How would you proceed? (*a*) Zinc oxide; (*b*) zinc chloride; (*c*) zinc sulfide.

6. Since magnesium compounds are so similar to calcium compounds, could you use magnesium hydroxide in place of calcium hydroxide in testing for carbon dioxide (§ 168)?

7. Why is it that a paint made from zinc oxide is not colored black by sulfur compounds?

8. What reaction, if any, would you expect if a strip of zinc were immersed in a solution of copper sulfate?

9. By what chemical test could you distinguish between soapstone and marble?

10. Lithopone is a mixture of barium sulfate and zinc sulfide. Is there any reason why a mixture of barium sulfide and zinc sulfate could not be used as lithopone?

11. Zinc oxide is often made by liberating zinc from its ores and then burning the zinc vapor in air. What weight of sphalerite would be required to make 6 tons of zinc oxide daily?

12. How many liters of hydrogen are liberated when 650 g. of zinc is dissolved (*a*) in hydrochloric acid? (*b*) in sulfuric acid?

FOR HONOR STUDENTS

1. Read one or both of the chapters listed below, and either write a theme on rubber or report the important facts orally: Chapter VIII (entitled "The Race for Rubber") in "Creative Chemistry"; Chapter XX (entitled "Chemistry in the Rubber Industry") in Volume I of "Chemistry in Industry."

2. Collect for your school museum a set of samples of the various substances that are used in making rubber tires (dealers in tires will help you to procure samples of pure rubber).

CHAPTER XXXIX

ALUMINUM

600. ***Introduction.*** The story of aluminum is a most interesting one. Discovered over a hundred years ago, it remained a curiosity for a long while, but was finally placed on the market at $90 per pound. Some improvement was made in the process used in its preparation, and in 1883 nearly 100 lb. were produced, worth about $5 per pound. At present the annual production exceeds 300,000,000 lb., and the price averages about 25 cents per pound.

This great increase in production has not been due to the discovery of new supplies of the metal, for its compounds are everywhere abundant; indeed, there is nearly twice as much aluminum in the earth's crust as iron (§ 23). The advance has been due entirely to the discovery of cheaper methods for separating the metal from its ores.

These methods were the outgrowth of the work of different investigators, including the American chemist Hall (Fig. 5). In 1886 Hall, then a student at Oberlin College, got the idea that it ought to be possible to separate aluminum by the process of electrolysis, and as a result of his investigations the method used today and known as the *Hall process* was devised.

601. Occurrence. Next to oxygen and silicon, aluminum is the most abundant of all the elements. The free element is not found in nature, but its compounds are widely distributed. The feldspars, which are the most abundant of the various minerals in the earth's crust, are all silicates of aluminum and either sodium, potassium, or calcium. Since the soil has been formed largely by the disintegration of these rocks, it is rich in the silicates of aluminum, chiefly in the form of clay (§ 430). Some of the other forms in which aluminum occurs in nature are the following: *corundum* (Al_2O_3); *emery* (Al_2O_3 colored black with oxide of iron); *cryolite* (Na_3AlF_6); *bauxite*, a mixture of hydrated aluminum oxides ($Al_2O_3 \cdot H_2O$ and $Al_2O_3 \cdot 3\ H_2O$) together with similar compounds of iron. Bauxite is the ore from which aluminum is prepared. In the United States it is found chiefly in Arkansas and Georgia.

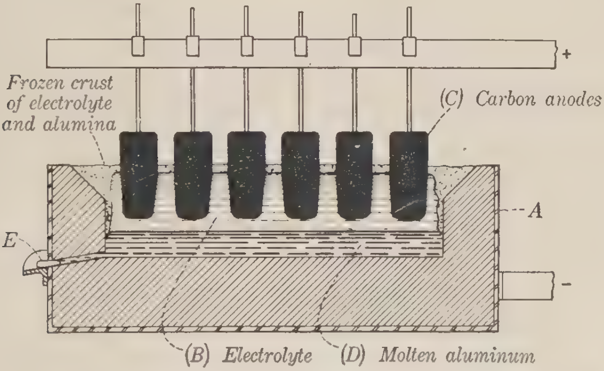


FIG. 274. The electrolytic production of aluminum

An iron box *A* is connected as cathode with a powerful electric generator, and a row of carbon anodes, *C*, dip into the box. Cryolite is melted in the box by its resistance to the current. Aluminum oxide, obtained from bauxite, is added from time to time and acts as an electrolyte, aluminum being liberated at the cathode and oxygen at the anodes. The temperature is kept above the melting point of aluminum, and the liquid metal collects under the lighter cryolite bath. The metal is drawn off at *E* from time to time

602. Preparation. The Hall process consists in the electrolysis of a solution of aluminum oxide (Al_2O_3) in melted cryolite. The aluminum oxide is prepared from bauxite. Some of the details of the Hall process are shown in Fig. 274.

It will be noted that the rather rare mineral bauxite, and not the very abundant clay, is used as the source of aluminum. No one has yet succeeded in finding an economical way of separating the metal from clay. Here is an opportunity for someone to make a discovery equal in value to that made by Hall.

603. Properties. Aluminum has many desirable properties. It is a silver-white metal, only about one third as heavy as iron, malleable, ductile, and fairly hard and strong. Moreover, it is a good conductor of heat and electricity. Neither air nor boiling water has any marked effect upon it. It is a good reducing agent, combining with oxygen with great evolution of heat. It dissolves easily in hydrochloric acid and concentrated sulfuric acid, but nitric acid has little action upon it. It is readily dissolved by alkalies and is corroded by salt water.

604. Uses. The facts that aluminum is light and strong and that it is not acted upon by air and water suggest many uses for this metal, either in the pure state or as an alloy. The use of the pure metal for making kitchen utensils of all kinds is well known. Since it is a good conductor of electricity, trolley and power wires are often made of it. Large amounts are used in the manufacture of steel. The largest use is in the automobile and aircraft industries, which consume about one third of the entire output of aluminum. In place of the pure metal, more often an alloy of the metal is used. Thus, the frames of airships and the wings and bodies of many airplanes are constructed of *duralumin*, an alloy of aluminum of variable composition; it generally contains, in addition to the aluminum, small percentages of copper, magnesium, and manganese. *Magnalium*, an alloy of aluminum and magnesium, is light and silver-white.

605. Goldschmidt reduction process. One of the general methods used for obtaining the metals from their ores is to reduce the oxides of the metals with carbon. The oxides of some metals cannot be reduced in this way because, as with calcium, they form carbides. In such cases we sometimes use powdered aluminum, since this is a powerful reducing agent — a method devised by the German chemist Goldschmidt. A great deal of heat is liberated in this reaction, so that the reduced metal is obtained in a molten state. Chromium, for example, is obtained in the free state according to the following equation:

$$Cr_2O_3 + 2\ Al \longrightarrow Al_2O_3 + 2\ Cr$$

606. Welding by use of aluminum. The powerful reducing property of aluminum is turned into practical account also in the welding of metals. This method may be illustrated by a single example, the welding of car rails, a process often carried out in connection with electric railways to secure good electrical connection. The ends of the rails are accurately aligned and thoroughly cleaned. A sand mold *A* (Fig. 275) is then clamped about the rail ends, sufficient space being left so that the metal can flow in. Just over the opening is placed the crucible *B*, which contains a mixture of iron oxide, and powdered aluminum. When the rail-ends have been heated to redness by the flame from a gasoline torch directed into the opening in the mold, the mixture in the crucible is ignited and the iron oxide is reduced to melted iron:

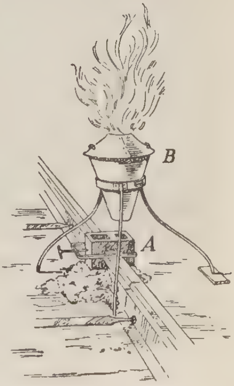


FIG. 275. Welding car rails with thermite

$$Fe_2O_3 + 2\ Al \longrightarrow Al_2O_3 + 2\ Fe$$

After a few seconds the crucible is opened at the bottom, and the molten iron resulting from the reaction is allowed to flow into the mold. In this way the molten metal surrounds the ends of the rails and, as it cools, joins them firmly together. A mixture of the metallic oxides and aluminum ready for use in welding is sold under the name of *thermite*.

The largest weld ever made was that of the sternpost of the army transport *Northern Pacific*, which was broken when the ship ran aground in a fog (Fig. 276).

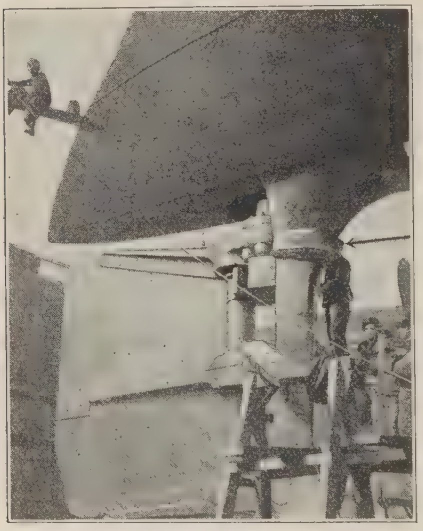


FIG. 276. View of the stern of the *Northern Pacific* showing the broken post after being welded by thermite (the break is at the point indicated by the arrow)

607. The compounds of aluminum. The metals so far studied are either univalent or bivalent. Aluminum is *trivalent*, and we must keep this in mind in writing the formulas of its compounds. Aluminum hydroxide is a very weak base (indeed, under some conditions it acts as an acid), so that the salts of aluminum hydrolyze (§ 551) with great ease; in fact most of the important uses of these salts, as in water purification, in the dye industry, and in baking powders, are based upon this property.

608. Aluminum oxide (Al_2O_3). This oxide occurs in several forms in nature. Corundum is a relatively pure form; emery, which we use for grinding and polishing, is a variety colored dark gray or black by iron compounds. In transparent crystals, tinted different colors by traces of impurities, it forms such precious stones as *sapphire, ruby, Oriental topaz*, as well as *Oriental amethyst*. All these varieties are very hard, being nearly as hard as the diamond. The cheaper forms, corundum and emery, are used for cutting and grinding. Chemically pure aluminum oxide can be made by igniting the hydroxide. The oxide so prepared is used in the preparation of aluminum. Some laboratory utensils, such as crucibles and tubes, are made of aluminum oxide, which is given the trade name *alundum*. The same material is used for cutting and polishing metals and alloys.

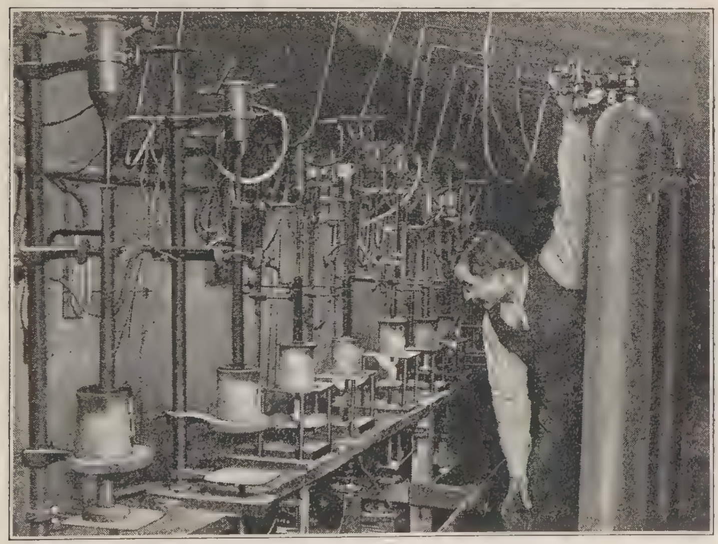


FIG. 277. A row of furnaces used in making artificial rubies

Oxygen is used to obtain high temperatures

609. Artificial gems. A number of gems are now prepared in the laboratory from melted aluminum oxide. The white sapphires so extensively advertised are simply the pure oxide. By fusing the oxide with small percentages of certain other metallic oxides (Fig. 277), different tints or colors are obtained, and in this way are prepared such gems as the ruby, the Oriental amethyst, and the yellow and blue sapphires, which are practically identical in composition and properties with the natural stones.

610. Aluminum hydroxide ($Al(OH)_3$). When ammonium hydroxide is added to a solution of any aluminum salt, there is precipitated a white gelatinous compound which we commonly regard as the hydroxide, $Al(OH)_3$:

$$AlCl_3 + 3\ NH_4OH \longrightarrow 3\ NH_4Cl + \underline{Al(OH)_3}$$

The precipitate formed does not always have this exact formula, but for our purposes it may be regarded as the pure hydroxide. The gelatinous character of the compound makes it useful in water purification, and also in the dye industry, as will be pointed out later.

611. Aluminum sulfate ($Al_2(SO_4)_3$). This compound is prepared by the action of sulfuric acid on bauxite. It crystallizes from water as $Al_2(SO_4)_3 \cdot 18\ H_2O$ under ordinary conditions. It is the cheapest of the soluble salts of aluminum, and is used as a source of aluminum hydroxide for the purification of water, for dyeing, and for the manufacture of certain kinds of paper.

612. Alums. Aluminum sulfate has the property of combining with the sulfates of the alkali metals to form compounds called *alums*. Thus, with potassium sulfate the reaction is expressed by the equation

$$K_2SO_4 + Al_2(SO_4)_3 + 24\ H_2O \longrightarrow 2\ (KAl(SO_4)_2 \cdot 12\ H_2O)$$

The sulfates of other trivalent metals can form similar compounds with the alkali sulfates, and these compounds are also called alums, though they contain no aluminum. They all crystallize in eight-sided crystals and contain 12 molecules of water of hydration. The alums most frequently prepared are the following:

Potassium alum	$KAl(SO_4)_2 \cdot 12\ H_2O$
Ammonium alum	$NH_4Al(SO_4)_2 \cdot 12\ H_2O$

613. Hydrolysis of salts of aluminum. While aluminum hydroxide forms fairly stable salts with strong acids, it is such a weak base that its salts with weak acids are readily hydrolyzed (§ 551). Thus, when an aluminum salt and a soluble carbonate are brought together in solution, we should expect to have aluminum carbonate precipitated according to the equation

$$Al_2(SO_4)_3 + 3\ Na_2CO_3 \longrightarrow Al_2(CO_3)_3 + 3\ Na_2SO_4$$

But if it is formed at all, it instantly begins to hydrolyze, the products of the hydrolysis being aluminum hydroxide and carbonic acid:

$$Al_2(CO_3)_3 + 6\ H_2O \longrightarrow 2\ Al(OH)_3 + 3\ H_2CO_3$$
$$H_2CO_3 \longrightarrow H_2O + CO_2$$

The property possessed by aluminum salts of liberating carbon dioxide from a carbonate is taken advantage of in the manufacture of certain fire extinguishers as well as in most of the baking powders now used.

614. Foam fire extinguishers. A common form of fire extinguisher known as the "foam" extinguisher is similar to that shown in Fig. 72 except that a solution of aluminum sulfate is used in place of sulfuric acid, the carbon dioxide being generated by the action of the aluminum compound on the sodium bicarbonate (§ 613). In addition the water present contains in solution some substance (such as an extract of licorice) which produces a foam when the carbon dioxide is generated. This foam consists of bubbles of the liquid filled with carbon dioxide. It is very effective in fighting oil fires (Fig. 278).

615. Aërating agents used in baking. In preparing foods made largely from dough, such as bread, biscuits, and cake, it is essential that some *aërating agent* be used to render the food light and wholesome. The aërating agent used is carbon dioxide generated in the dough. The following methods are used for generating the gas in baking:

1. ***By alcoholic fermentation.*** As we have seen, this is the method generally used in making bread (§ 503).

2. ***By the action of sour milk on sodium bicarbonate.*** The lactic acid present in the sour milk (§ 486) slowly acts upon the bicarbonate, liberating carbon dioxide:

$$H \cdot C_3H_5O_3 + NaHCO_3 \longrightarrow NaC_3H_5O_3 + H_2O + CO_2$$

3. ***By the action of an acid salt or alum upon sodium bicarbonate; baking powders.*** Every baking powder contains three ingredients, as follows: (1) sodium bicarbonate to furnish the carbon dioxide; (2) some compound which in the presence of water reacts with the bicarbonate and slowly liberates carbon dioxide; and (3) starch or flour, which keeps the powder dry by absorbing moisture and hence prevents deterioration. The compounds used for liberating the carbon dioxide from the bicarbonate are either (*a*) cream of tartar, sometimes mixed with tartaric acid (§ 509), (*b*) an acid phosphate, generally $CaH_4(PO_4)_2 \cdot H_2O$, or (*c*) sodium aluminum sulfate ($Na_2SO_4 \cdot Al_2(SO_4)_3$) commonly referred to as S.A.S. Often a mixture of the acid phosphate and sodium aluminum sulfate is used. A baking powder is generally designated by the name of the compound used to liberate the carbon dioxide.

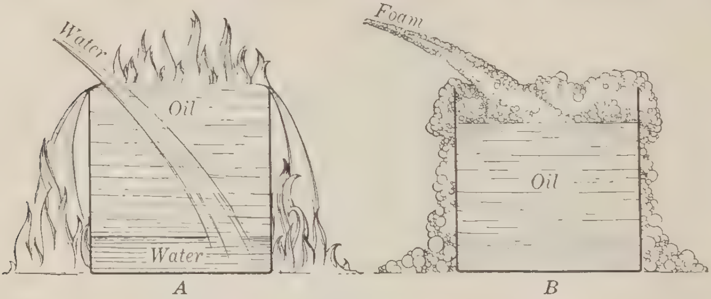


FIG. 278. The comparative use of water and "foam" in extinguishing fires

The water, *A*, does not mix with the oil, and being heavier than the oil sinks to the bottom, so that the oil continues to burn. The "foam," *B*, on the other hand, floats on the oil and smothers the flame by preventing the oxygen of the air from coming into contact with the oil

The reactions that take place when water is added to each of the above classes of baking powders are represented in the following equations:

Cream of tartar:

$$KHC_4H_4O_6 + NaHCO_3 \longrightarrow KNaC_4H_4O_6 + H_2O + CO_2$$

Phosphate:

$$CaH_4(PO_4)_2 + 2\,NaHCO_3 \longrightarrow CaHPO_4 + Na_2HPO_4 + 2\,H_2O + 2\,CO_2$$

Sodium aluminum sulfate:

$$Na_2SO_4 \cdot Al_2(SO_4)_3 + 6\,NaHCO_3 \longrightarrow 2\,Al(OH)_3 + 4\,Na_2SO_4 + 6\,CO_2$$

Dyes and Dyeing

616. Properties of dyes. We have already learned (§ 521) something of the aniline dyes and the history of their discovery. Because of their very great coloring power these dyes have almost entirely taken the place of the dyes extracted from plants and trees (Fig. 279).

The requisites of a good dye are as follows: (1) it must have an acceptable color; (2) it must not injure the fabrics; (3) it must *dye fast,* or in other words the cloth after having been dyed must retain its color when washed with water; (4) it must not fade too easily.

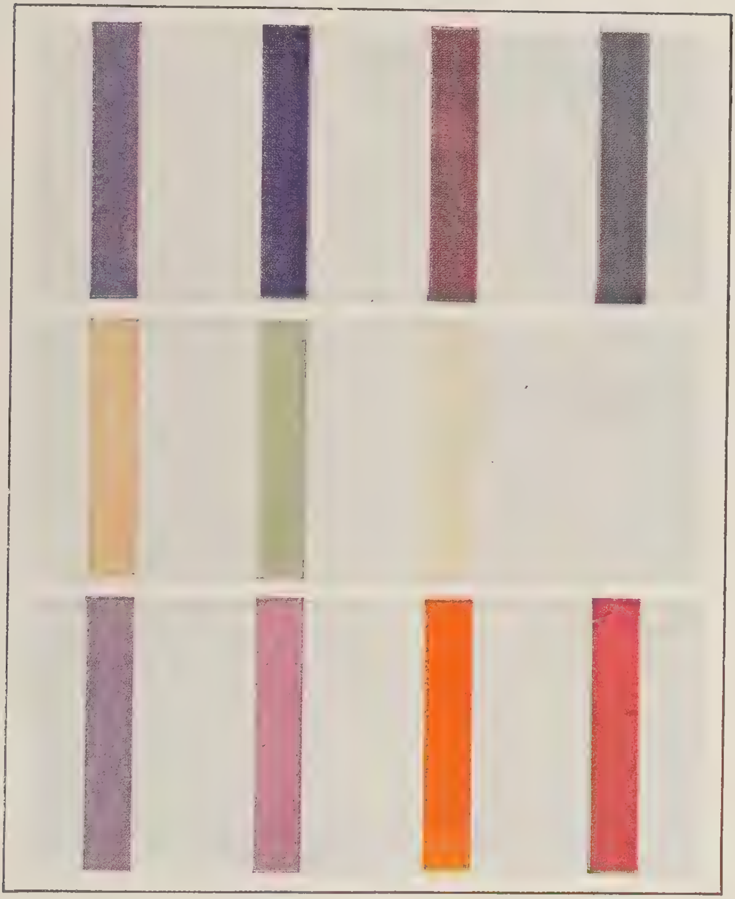
617. The process of dyeing. This process consists in fixing the dye uniformly upon the fabric. The animal fibers, wool and silk, are as a rule more readily dyed than cotton, which is a vegetable fiber. To dye wool and silk with most dyes it is only necessary to steep the fabric in a solution of the dye. Cotton fabrics, when treated in this way, will become colored, but with most dyes the color is not *fast.* Cotton fabrics may be dyed fast in the following way:

The cloth is first soaked in a solution of an aluminum salt (or a similar substance), which readily undergoes hydrolysis. The cloth is then exposed to the action of steam, which hydrolyzes the salt, leaving the colloidal hydroxide thoroughly incorporated in the fiber. The cloth is then steeped in the dye, which is adsorbed by the aluminum hydroxide and is in consequence fastened, or "fixed," upon the fiber. Aluminum hydroxide and other substances which act in the same way are called *mordants*. The same dye will often give different colors with different mordants, as shown upon the accompanying colored plate.

FIG. 279. Interior of an indigo factory

Indigo, one of our most common dyes, was formerly obtained from a plant grown largely in India. Now it is made from coal tar (benzene) at a lower cost

The compounds which serve well as mordants may be precipitated in solutions containing various dyes, and the precipitate will be highly colored, though not always of the same color as the dye. Colored precipitates of this kind are called *lakes* and are used as pigments in paints.



Iron Chromium Tin Aluminum

THE USE OF MORDANTS IN DYEING

The central panel in the figure represents a piece of white cotton cloth. A mordant of iron, of chromium, of tin, and of aluminum has been applied to the cloth in four vertical stripes (leaving the spaces between without a mordant). The upper panel shows the same cloth after being dyed with gallein; the lower panel shows a similar piece of cloth after being dyed with alizarin

CHAPTER SUMMARY IN QUESTION FORM

1. Aluminum, formerly selling at $90 or more per pound, is now worth about 25 cents per pound. Name the man, the process, and the compound largely responsible for this reduction in price.

2. (*a*) Name four forms in which aluminum occurs in nature. (*b*) Which of these are used in the commercial production of aluminum?

3. Why is aluminum prepared from the rather rare mineral bauxite, in place of clay, which is everywhere abundant?

4. Name five properties of aluminum that make it so valuable for many uses.

5. (*a*) Name the alloy that is so largely used in the construction of airships and airplanes. (*b*) What metals are present in this alloy?

6. What property have aluminum and carbon in common that make them useful in separating metals from their ores?

7. Aluminum is much more expensive than carbon. Why, then, is it sometimes used rather than carbon in separating metals from their ores?

8. (*a*) What is thermite, and (*b*) for what is it used?

9. (*a*) State the valence of aluminum, and (*b*) write the formulas for the normal aluminum salt of each of the following acids: hydrochloric, sulfuric, and phosphoric.

10. Aluminum hydroxide is a very weak base. Would you expect the salts of aluminum to hydrolyze readily?

11. (*a*) What compound is formed when ammonium hydroxide is added to a solution of any aluminum salt? (*b*) The gelatinous character of the compound formed makes the compound useful for what purposes?

12. Give the name and formula for the cheapest of the soluble compounds of aluminum.

13. (*a*) Give the name and formula of a common alum. (*b*) Do all alums contain aluminum?

14. When a solution of sodium carbonate is added to a solution of an aluminum salt such as aluminum sulfate, carbon dioxide is evolved. Account for the formation of this gas by writing the equations for the reactions that take place between sodium carbonate and aluminum sulfate.

15. What use is made of the fact that carbon dioxide is evolved in the reaction referred to in question 14?

16. (*a*) Name three methods for aërating dough. (*b*) What is the aërating agent in each of these methods?

17. Name three substances present in all baking powders, and the use of each.

18. Name the four requisites of a good dye.

19. Tell what is meant by the words (*a*) lake, (*b*) mordant.

THOUGHT QUESTIONS

1. Name two important chemical discoveries made by young men.

2. Why do the directions for using aluminum cooking vessels state that such utensils should not be washed with strong soaps?

3. When baking soda is heated, carbon dioxide is evolved (§ 547). Why not, then, use it alone as an aërating agent?

4. Does the question as to whether a baking powder is injurious to health depend only on the compounds that constitute the powder?

5. What compounds remain in biscuits as a result of the use of each of the different kinds of baking powders?

6. (*a*) Would a mixture of sweet milk and soda serve just as well as a mixture of sour milk and soda as an aërating agent? (*b*) Give reason for your answer.

7. What is the difference between baking powder and baking soda?

8. Can you suggest any reason why baking powder is not used in baking loaves of bread?

9. Do you think that a mixture of baking soda and the juice of grape fruit would act as an aërating agent?

10. Which should you expect to hydrolyze the more readily, aluminum sulfate or aluminum carbonate?

11. Should you expect a water solution of aluminum sulfate to be acid, neutral, or basic?

12. An aluminum plant has a daily output of 20,000 kg. of the metal daily. What weight of aluminum oxide would be required daily?

13. What weight of water of hydration is present in 1 kg. of potassium alum?

14. (*a*) What is the ratio between the number of gram-molecular weights of baking soda used in a baking powder and the number of gram-molecular weights of carbon dioxide liberated (see equations, § 615)? (*b*) Calculate the volume of carbon dioxide liberated from 1 gram-molecular weight of baking soda if the temperature of the gas is 150°. (For method of changing volume at 0° to volume at 150°, see § 69.)

FOR HONOR STUDENTS

1. Ordinary cream-of-tartar baking powders contain about 12 per cent of starch or flour, the other 88 per cent consisting of baking soda and cream of tartar mixed in the proper proportions. Refer to the equation for the reaction of cream-of-tartar baking powders (§ 615, 3), and calculate the number of grams of (*a*) starch, (*b*) baking soda, and (*c*) cream of tartar required to make 500 g. of baking powder. Obtain the required weights of the pure substances and make, say, 500 g. of the powder for use in your home. (The ingredients must be thoroughly mixed.)

2. Read one or both of the chapters listed, and write a theme on the general subject of "Dyes and Dyeing": Chapter IV (entitled "Coal-tar Colors") in "Creative Chemistry"; Chapter IV (entitled "The Chemical Rainbow") in Volume II of "Chemistry in Industry."

CHAPTER XL

HOW WE PURIFY AND SOFTEN NATURAL WATERS ON A LARGE SCALE

618. ***Introduction.*** Earlier in our study (Chap. VI) we learned that all natural waters contain more or less mineral and organic matter, dissolved from the soil and rocks. The mineral matter wastes lots of soap and causes trouble in steam boilers (§ 587), but it is not often injurious to health. On the other hand we have learned that the organic matter must always be regarded with suspicion, for it is apt to contain disease-producing organisms (bacteria, Fig. 280) that have found their way into the water supply through sewage from persons afflicted with certain diseases.

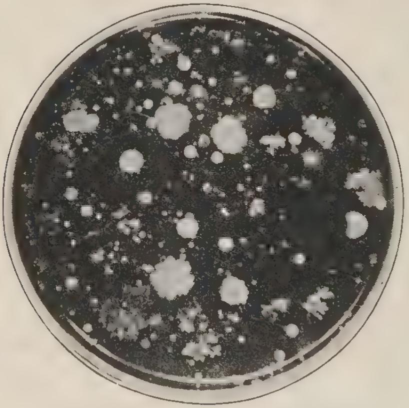


FIG. 280. Bacteria in impure water

Colonies of bacteria growing in gelatin to which a few drops of water have been added. Each colony corresponds to a single bacterium in the original water

Most cities and towns must obtain their water supply from lakes and rivers, and with increasing population it is impossible to prevent contamination of such waters. As a result practically all our towns and cities now find it necessary to purify their entire water supply; otherwise outbreaks of diseases such as typhoid fever are sure to occur. The effects of such purification in diminishing the deaths from typhoid fever in a typical city are shown in Fig. 42.

619. Methods used in purifying water on a large scale. The average consumption of water in our cities amounts to about 100 gal. daily for each person, so that the total daily consumption in a city of any size runs into many millions of gallons. Of course it is idle to think of purifying such volumes by distillation or boiling. New methods have had to be devised, and the following are the ones now used:

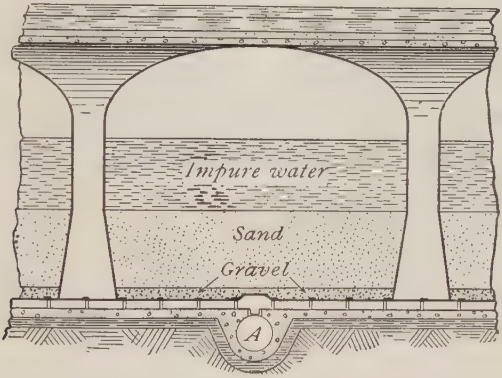


FIG. 281. A covered slow sand filter for purifying water on a large scale

The purified water passes into the porous pipe *A*, from which it is pumped into the city mains

1. ***Treatment with chlorine alone.*** This is the simplest method, but it can be effectively employed only when the natural water used is clear, as is the case in Chicago and New York. Ordinarily the pure chlorine is added directly (Fig. 283), although in some instances bleaching powder is used as a source of chlorine.

2. ***Filtration through slow sand filters and subsequent treatment with chlorine.*** These filters are constructed of sand and gravel, as shown in Fig. 281. Some of the impurities

are strained out by the filter, while others are decomposed by certain kinds of bacteria which collect in a jelly-like layer on the surface of the filter. Chlorine is added to the filtered water as an extra precaution.

3. ***Treatment with aluminum sulfate (or ferrous sulfate), filtration, and subsequent treatment with chlorine.*** Most of our natural waters are slightly basic in character. If aluminum sulfate is mixed with such waters, aluminum hydroxide is formed (§ 613) as a colloidal dispersion throughout the water. This slowly coagulates, and, as it settles, carries down with it any suspended matter that is present (Fig. 282), including bacteria and coloring materials. After the precipitate has settled, the relatively clear water is drawn off and run through rapid sand filters. It is then treated with a small amount of chlorine as a final precaution. The rapid sand filters are made of sand and gravel (*H*, Fig. 285) and are largely replacing the slow sand filters, since they are much less expensive and are equally effective when used with water which has been treated with aluminum sulfate as described above.

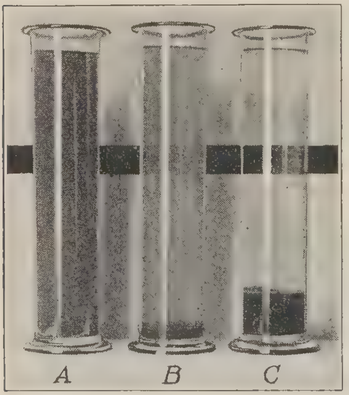


FIG. 282. Purification of water by aluminum sulfate

Cylinder *A* contains impure water before treatment. In cylinder *B* some aluminum sulfate has been added and the resulting aluminum hydroxide, together with suspended impurities, is slowly settling. In cylinder *C* the settling is complete

620. Hard waters. We speak of water that contains any large percentage of mineral matter as *hard water*. The mineral matter present in most of our natural waters consists of calcium and magnesium, present either in the form

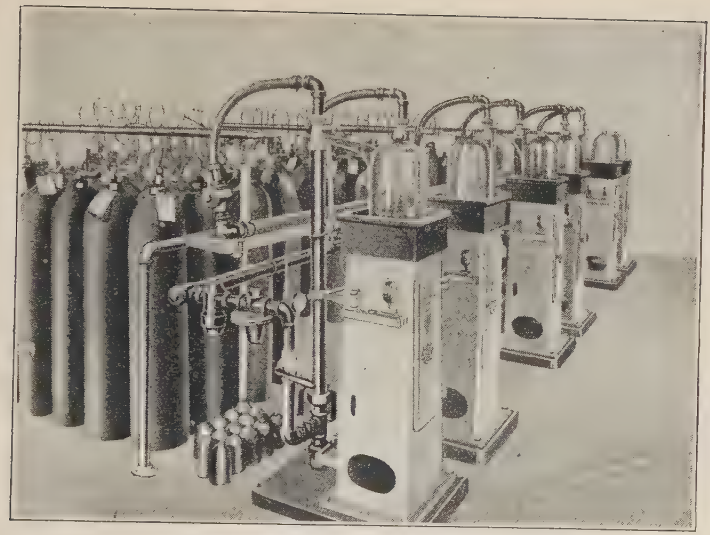


FIG. 283. Water purification by treatment with chlorine

The chlorine is led from the bombs in which it is stored into the water

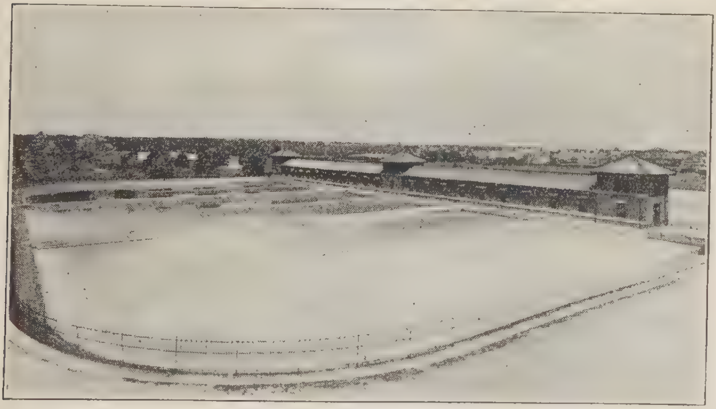


FIG. 284. View of the settling basin at the water works, Columbus, Ohio

The water, mixed with the purifying and softening chemicals, flows into the basin in the foreground and then slowly flows back and forth between the tiers until it reaches the rear of the basin, by which time all the solid materials have settled, leaving the water clear, soft, and pure

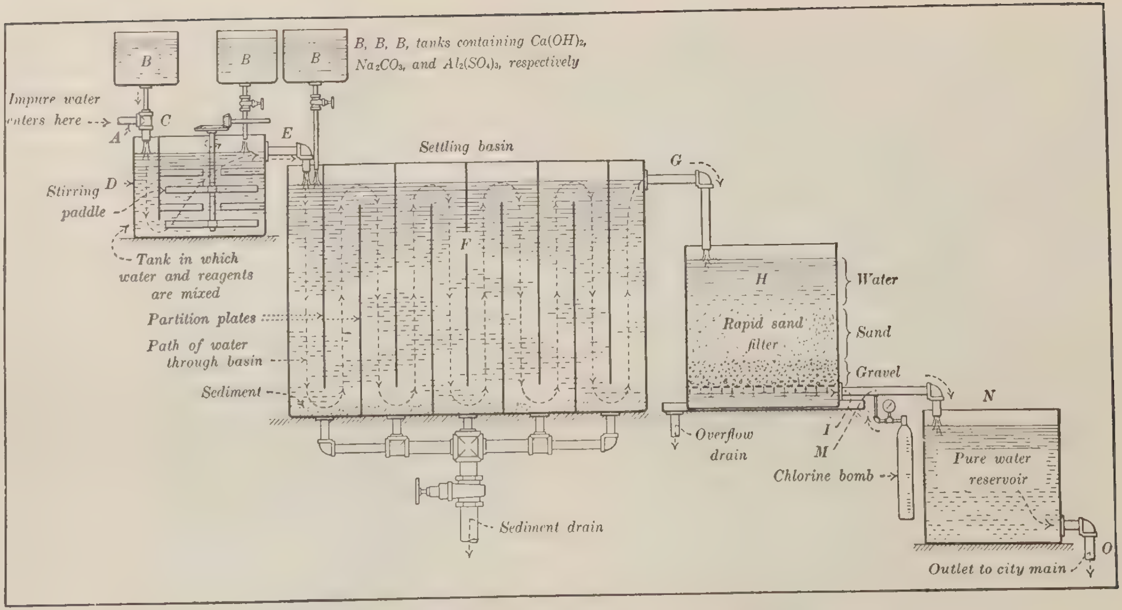

B
B
B
B, B, B, tanks containing $Ca(OH)_2$, Na_2CO_3, and $Al_2(SO_4)_3$, respectively
Impure water
nters here
C
A
E
Settling basin
G
Stirring
paddle
D
Tank in which water and reagents are mixed
F
Partition plates
Path of water through basin
Sediment
H
Water
Rapid sand filter
Sand
Gravel
N
Overflow drain
I
M
Chlorine bomb
Pure water reservoir
Sediment drain
O
Outlet to city main

FIG. 285. Diagram showing how water is softened and purified

The impure water enters at *A*, and the purifying and softening chemicals flow into it from the tanks *B*, *B*, *B*. The mixture then flows into the settling basin *F*. The impurities settle to the bottom of the basin and are drawn off from time to time. The purified water then flows through the rapid sand filter *H*. As it passes out, the necessary chlorine is added at *M*. The pure water then flows into the pure-water reservoir and from this into the city mains of their acid carbonates, $Ca(HCO_3)_2$, $Mg(HCO_3)_2$, or in the form of their sulfates and chlorides. Water that contains the acid carbonates of calcium and magnesium is said to have *temporary hardness*. Such waters can be softened by boiling, since the acid carbonate is decomposed by heat, forming the insoluble normal carbonates (§ 568). On the other hand, water that contains the sulfates or chlorides of calcium and magnesium is said to have *permanent hardness*. Such waters cannot be softened by boiling.

621. How hard waters are softened. Since most of our city water supplies are hard waters, it becomes a great saving in our homes and in our factories — in soap, in boiler scale, in deposits in hot-water pipes — to have the mineral matter removed from such waters, or, in other words, to have the water *softened*. The processes of purification and of softening may be carried on together. The method used is the same as method 3 described above for purifying waters, except that along with the aluminum sulfate the requisite quantities of calcium hydroxide and sodium carbonate are added. That portion of the calcium and magnesium present as acid carbonates is precipitated by the calcium hydroxide, while that present as chlorides and sulfates is precipitated by the sodium carbonate. These reactions are expressed in the following equations (using calcium as the example, since calcium and magnesium act in the same way):

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2\ \underline{CaCO_3} + 2\ H_2O$$

$$CaSO_4 + Na_2CO_3 \longrightarrow \underline{CaCO_3} + Na_2SO_4$$

$$CaCl_2 + Na_2CO_3 \longrightarrow \underline{CaCO_3} + 2\ NaCl$$

The normal calcium and magnesium carbonates formed are practically insoluble and settle out as the water slowly flows through reservoirs known as *settling basins* (Fig. 284). It is evident from the equations given above that waters softened by this process will contain sodium sulfate and sodium chloride, but the presence of these salts is not objectionable. Fig. 285 shows how the processes of purifying and softening water are carried out on a large scale.

Some idea of the economy resulting from the softening of the city water supply may be inferred from the fact that it is estimated that the softening of the city water in Columbus, Ohio, has effected a saving in soap alone amounting annually to $250,000, to say nothing of the money that would otherwise be spent in the construction of cisterns and small water-softening plants for homes and factories.

622. The zeolite process for softening water. The name *zeolite* is given to a mixture of complex sodium-aluminum silicates found in nature and also prepared in the laboratory and used in softening water.

If hard water is passed through a container filled with finely divided zeolite, the calcium and magnesium present in the water replace the sodium in the zeolite and are thus withdrawn from the water, leaving a *soft* water:

$$Na_2O \cdot Al_2O_3 \cdot 2\,SiO_2 + CaCl_2 \rightleftarrows CaO \cdot Al_2O_3 \cdot 2\,SiO_2 + 2\,NaCl$$

When the sodium in the zeolite has been replaced, the resulting calcium compound is treated with a saturated solution of sodium chloride. The reaction is then reversed (mass action, § 311) and the regenerated zeolite is ready for use once more.

CHAPTER SUMMARY IN QUESTION FORM

1. State the two kinds of impurities present in natural waters, and the effect of each when such waters are used (*a*) for cleansing and industrial purposes; (*b*) for drinking.

2. Is it ever necessary to purify or to soften natural waters that are perfectly clear and odorless?

3. Is chlorine used to soften water or to purify it?

4. What reaction takes place when aluminum sulfate is added to most natural waters?

5. What compounds present in a natural water make it (*a*) a temporary hard water? (*b*) a permanent hard water?

6. May the same water be both a temporary and a permanent hard water?

7. Write an equation for a reaction that may be used for softening a temporary hard water (*a*) in our homes; (*b*) in our city water supply.

8. Write an equation representing the reaction that may be used for softening permanent hard water.

9. Why does the presence of calcium ions and magnesium ions in water make it costly to use for laundry purposes?

10. In the zeolite process for softening water, the ions of what metal are used to replace the objectionable calcium and magnesium ions in the water?

THOUGHT QUESTIONS

1. What property has chlorine that makes it efficient in water purification?

2. Explain how it is possible to remove calcium compounds from temporary hard water by adding more calcium compounds.

3. (*a*) What is the chemical composition of soap? (*b*) Explain why calcium and magnesium compounds in waters consume so much soap, while compounds of sodium do not.

FOR HONOR STUDENTS

1. Visit the office in charge of the water supply of your city or town, find out the following facts, and report on them: (*a*) source of the water supply; (*b*) gravity or pumping system; (*c*) method of purification used; (*d*) if water is softened, method used.

2. A certain city uses 30,000,000 gal. of water daily, and 100 gal. of the water contain 120 g. of calcium acid carbonate and 30 g. of calcium sulfate. Calculate the weights of calcium hydroxide and sodium carbonate required to soften the daily water supply.

3. Read Chapter XXII (entitled "The Relation of Chemistry to Water Supplies") in Volume II of "Chemistry in Industry," and report to the class the facts that interest you most.

CHAPTER XLI

IRON AND TWO CLOSELY RELATED METALS

623. *Introduction.* If the student turns to the periodic table (p. 289) he will see that after manganese, of atomic number 25, come three elements — iron, cobalt, and nickel — that do not fit into the general plan of the periodic law and are placed together in an extra group (VIII). These three elements have atomic weights very near together and resemble each other closely in many ways — in appearance, melting points, densities, and chemical conduct. We may call them the iron "family," though they do not constitute a family in the same sense as that in which we have been using that word. It should be noted that there are two other families of this same kind in Group VIII, of three metals each.

Iron

The Most Used Metal in the World

624. General. We have learned that oxygen is the most abundant element, but if we knew all about the world we should probably find that iron greatly exceeds oxygen. The meteorites that fall on the earth are largely iron, and the average density of the earth makes it seem probable that its interior is largely iron. If we count only the crust of the earth, iron ranks fourth in abundance.

With the exception of meteorites, iron does not occur free in nature, yet it has been known and widely used as a metal for at least four thousand years. This shows that its ores must be abundant, and that the metal is easily produced from them.

Iron is peculiar in that the *pure* metal has relatively few uses and is rarely prepared. Even very small percentages of other elements, especially carbon, greatly modify the properties of iron and make it much more useful. So nearly all commercial iron is really an alloy, though sometimes the alloy material does not exceed a few tenths of 1 per cent.

625. Occurrence. Iron occurs in large deposits as oxides, sulfides, and carbonates, and in smaller quantities in a great variety of minerals. Indeed, very few rocks or soils are free from small percentages of iron, and their colors are largely due to the iron in them. As a constituent of the hemoglobin of the blood of animals it plays an important part in life processes.

626. Pure iron. Pure iron can be prepared by electrolysis of iron salts, or by the reduction of iron oxide by hydrogen; but it is of little commercial importance. It is a silvery metal which melts at 1535°. It is ductile and malleable and is almost as soft as aluminum.

627. Iron of commerce. In the iron of commerce carbon is always present in amounts which vary from a mere trace to about 5 per cent. According to the condition of treatment, the carbon may be in the form of graphite scattered through the iron, or it may occur dissolved in the iron, or it may be combined with the iron as a carbide. One of the most important of these carbides is the one that has the formula Fe_3C and is called *cementite.* Manganese, silicon, and traces of phosphorus and sulfur, together with a little oxygen, are also likely to be present.

The properties of the iron are greatly modified by the percentages of these elements, by their form of combination, and by the treatment of the metal during its production. The result is that we have many varieties of iron. The most common varieties recognized in commerce are the well-known forms called *cast iron, wrought iron,* and *steel.*

628. Materials used in metallurgy of iron. Four classes of materials are used in the metallurgy of iron:

1. ***Iron ore.*** The ores most frequently employed are the following:

Hematite	Fe_2O_3	Siderite	$FeCO_3$
Magnetite	Fe_3O_4	Limonite . . .	$2\ Fe_2O_3 \cdot 3\ H_2O$

While iron ore is mined in a number of different localities in the United States, the great center of production is in the neighborhood of Lake Superior, the ore being chiefly hematite. Large amounts are also mined near Birmingham, Alabama. Fig. 286 represents one of the large mines in Minnesota.

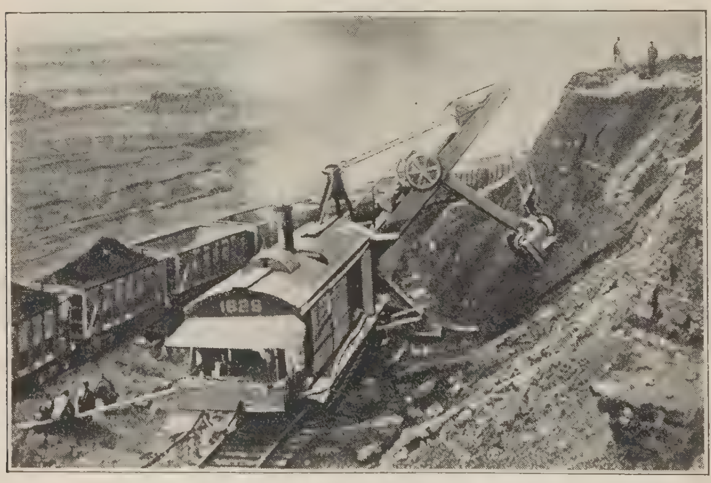


FIG. 286. Mining iron ore in Minnesota

2. ***Carbon.*** Carbon in some form is necessary both as a fuel and as a reducing agent. In former times wood charcoal was used to supply the carbon, but now coke is almost universally used.

3. ***Heated air.*** To maintain the high temperature required for the reduction of iron, a very active combustion of fuel

is necessary. This is secured by forcing a strong blast of air into the lower part of the furnace during the reduction process, the air being *previously heated* to increase the temperature of the combustion.

4. ***Flux.*** All the materials which enter the furnace must leave it again, in the form of either gases or liquids. The iron is drawn off as the liquid metal after its reduction, the oxygen with which it was combined escaping as oxides of carbon. Both the ore and the coke contain earthy matter that under ordinary conditions would be left as solid ash and clog the furnace. This material is usually rich in silica and aluminum. To get rid of it, limestone is added along with the ore, and the ash and the limestone together produce a high-melting liquid glass, which flows out of the furnace after the heavier iron has been withdrawn. The material added, usually limestone, is called the *flux*; the liquid glass is called *slag*.

629. Cast iron. Ordinarily the first step in the manufacture of any variety of commercial iron is the production of *cast iron.* The ores are mixed with a suitable flux and are reduced by heating with coke. The chief reaction is

$$Fe_2O_3 + 3\,CO \longrightarrow 2\,Fe + 3\,CO_2$$

The reduction is carried out in a large tower called a *blast furnace* (Fig. 287).

630. Blast-furnace process. The blast furnace is usually 80 ft. high and 20 ft. in internal diameter at its widest part, narrowing somewhat toward both the top and the bottom. The walls are built of steel and are lined with fire brick. The base is provided with a number of pipes *B*, called *tuyères*, through which hot air is forced into the furnace. The tuyères are supplied from a large pipe *A*, which girdles the furnace. At the base of the furnace is an opening *C*, through which the liquid metal can be drawn off from time to time. There is also a second opening *D*, somewhat above the first, through which the excess of slag overflows. The top is closed by a movable trap *G*, called the *bell*, and through this the materials to be used are introduced. The gases resulting from the combustion of the fuel and the reduction of the ore, together with the nitrogen of the air admitted through the tuyères, leave the furnace through the pipe *E*. These gases are very hot and contain a sufficient percentage of carbon monoxide to render them combustible; they are accordingly utilized for heating the blast of air admitted through the tuyères and as fuel for the engines.

Charges consisting of coke, ore, and flux in proper proportion are at intervals introduced into the furnace through the bell. At the bottom of the furnace the coke burns fiercely in the hot-air blast, forming carbon dioxide, which is at once reduced to carbon monoxide as it passes over the highly heated carbon.

Reduction of the ore begins at the top of the furnace (the coolest part) through the action of the carbon monoxide. As the ore slowly descends the reduction is completed, and the resulting iron melts and collects as a liquid in the bottom of the furnace, the lighter slag floating above it. After a considerable quantity of iron has collected, the slag is drawn off through *D*. The molten iron is then run into large ladles (Fig. 288, *A*), and either used directly in the manufacture of steel or cast into sticks known as pigs.

In practice a number of furnaces are usually operated together, as illustrated in Fig. 289, which shows an exterior view of a modern plant for making cast iron.

631. Properties of cast iron. The iron produced in the blast furnace is called *cast iron*. It varies considerably in composition, but always contains over 2 per cent of carbon, variable amounts of silicon, and at least traces of sulfur, together with all the phosphorus originally present in the ore and coke. The form in which the carbon is present, whether free or combined, greatly modifies the properties

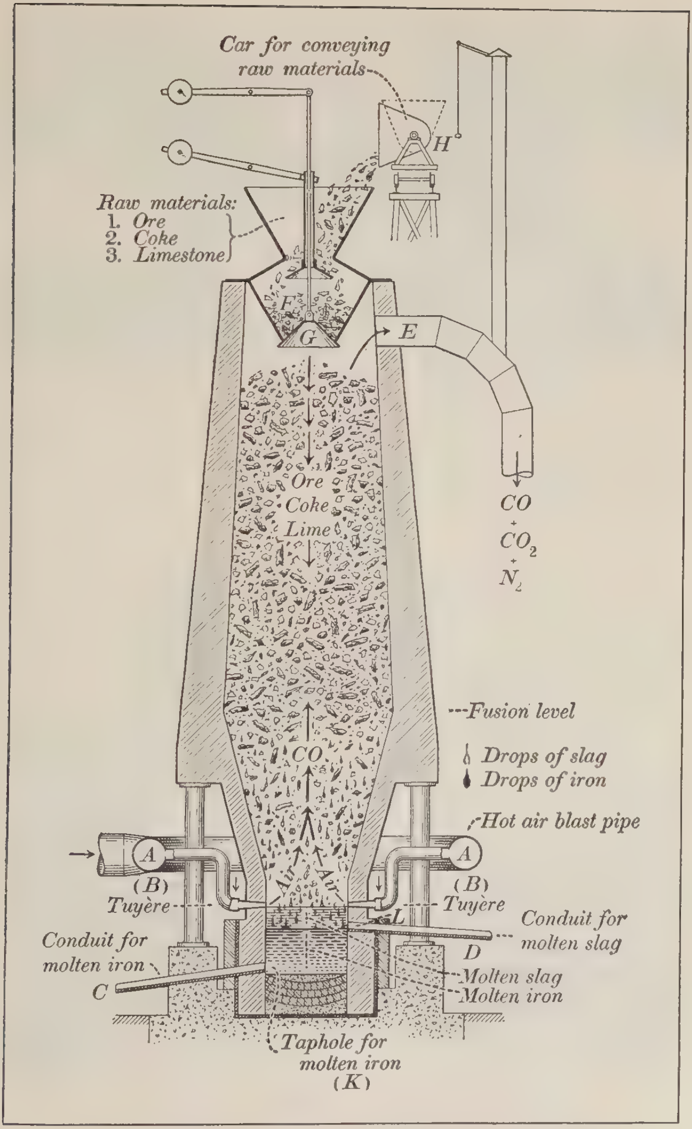

Car for conveying raw materials
H
Raw materials:
1. Ore
2. Coke
3. Limestone
F
G
E
Ore
Coke
Lime
CO
CO
+
CO2
+
N2
Fusion level
Drops of slag
Drops of iron
Hot air blast pipe
A
A
(B)
(B)
Air
Air
Tuyère
Tuyère
L
Conduit for molten slag
D
Conduit for molten iron
C
Molten slag
Molten iron
Taphole for molten iron
(K)

FIG. 287. Vertical section of a typical blast furnace

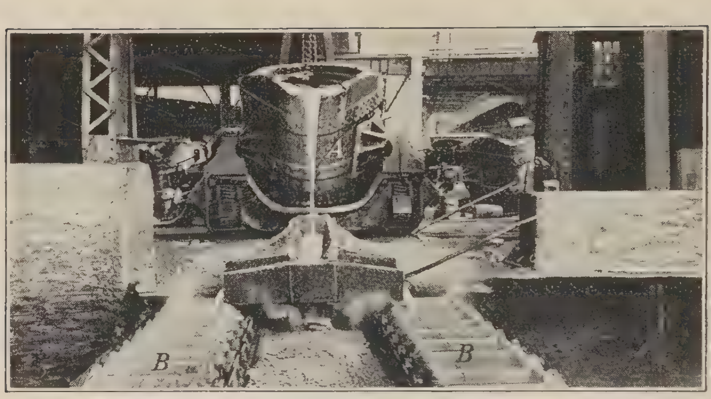


FIG. 288. Casting pig iron from a blast furnace

Liquid iron is poured from the ladles into iron troughs *B*, *B*, or molds lined with lime. These troughs are attached so as to form an endless belt. The molten iron in each trough solidifies by the time it reaches the farthest point; and as the belt reverses, the solid pieces of iron fall into cars placed beneath it

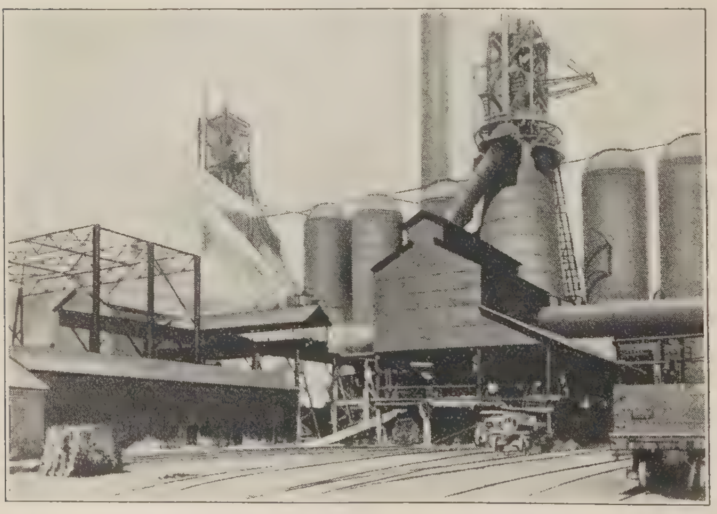


FIG. 289. Exterior view of a row of blast furnaces

In practice a number of blast furnaces usually constitute one plant, as shown in the illustration of the iron. In general, cast iron is hard and brittle and melts at about 1100°. It cannot be welded or forged, but is easily cast in sand molds. It is rigid, but not elastic, and its tensile strength is small. It is used for making castings such as steam radiators or parts of stoves, but chiefly as a starting-point in the manufacture of other varieties of iron.

632. Wrought iron. Wrought iron is made from cast iron by burning out most of the carbon, silicon, phosphorus, and sulfur, the operation being conducted in what is called a *puddling furnace.*

Wrought iron is soft, malleable, and ductile. Its tensile strength is greater than that of cast iron, but less than that of most steel. Its melting point is much higher than that of cast iron. It is no longer produced to the same relative extent as in former years, since soft steel can be made at a less cost and has almost the same properties.

633. Steel. Steel, like wrought iron, is made from cast iron by burning out a part of the carbon, silicon, phosphorus, and sulfur, but the processes used are quite different from the one employed in the manufacture of wrought iron. Nearly all the steel of commerce produced in the United States is made by one of two general methods, known as the *acid Bessemer process* and the *basic open-hearth process.*

634. Acid Bessemer process. In the acid Bessemer process the furnaces used, called *converters* (Figs. 290 and 291), are lined with *silica,* which, it will be recalled, is an *acid anhydride;* this explains the name of the process. These furnaces remove from the cast iron the carbon and silicon but not the phosphorus and sulfur. *The process is therefore employed when the cast iron to be used is low in phosphorus and sulfur.*

635. Details of the Bessemer process. This process, invented about 1860, is carried out in great egg-shaped *converters* (Fig. 290), one of which often holds 25 tons of steel. The converter is built of steel and lined with silica. It is mounted on axles, or *trunnions*, so that it can be tipped over on its side for filling and emptying. One of the trunnions is hollow, and a pipe connects it with an air chamber *A*, which forms a false bottom to the converter. The true bottom is perforated so that air can be forced in by an air blast admitted through the trunnion and the air chamber.

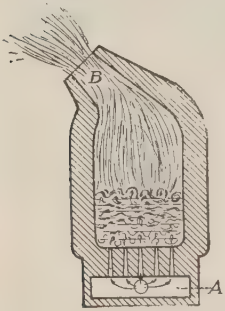


FIG. 290. Vertical section showing details of a Bessemer converter

White-hot liquid cast iron from a blast furnace is run into the converter through its open necklike top *B*, the converter being tipped over to receive it; the air blast is then turned on and the converter turned to a nearly vertical position. The carbon and silicon in the iron are rapidly oxidized (first the silicon and then the carbon), the oxidation being attended by a brilliant flame (Fig. 291). The heat of the reaction, largely due to the combustion of silicon, keeps the iron in a molten condition. The air blast is continued until the character of the flame shows that all the carbon has been burned away. The process requires from fifteen to twenty minutes, and when it is complete the desired quantity of carbon (generally in the form of high-carbon iron alloy) is added and allowed to mix thoroughly with the fluid. The converter is then tilted and the steel run into molds (*D*, Fig. 294), and the ingots so formed are hammered or rolled into rails or other objects.

636. Basic open-hearth process. The presence of more than traces of phosphorus and sulfur in finished steel renders the metal so brittle that it is worthless for most purposes. In the basic open-hearth process (Fig. 292), in which the lining of the furnace is made of limestone or dolomite, both of which act as *bases*, the phosphorus and sulfur are both removed, as well as the silicon and carbon. The open-hearth process therefore possesses a great advantage over the acid Bessemer process in that it makes it possible to use iron ores (or cast iron obtained from them) that contain appreciable quantities of phosphorus and sulfur. The operation does not need to be hastened, and steel of any desired composition can be produced. An average furnace produces about fifty tons of steel in one operation, approximately eight hours being required in the process.

In the open-hearth process cast iron is introduced into long, low furnaces (Fig. 292) lined with limestone or dolomite and heated with a long gas flame that is reflected by the roof of the furnace upon the surface of the iron. Such a furnace is called a *reverberatory* furnace because the heat is reflected downward by the roof. Flames from sprayed oil or finely powdered coal are also used. The carbon present is oxidized and escapes as gas. The silicon, phosphorus, and sulfur are also oxidized, and the resulting oxides combine with some of the lime lining to form a slag which floats on the surface of the steel and is easily removed. When the operation is complete the liquid steel is drawn off (Fig. 294) and cast into the form of ingots (Figs. 294, 295). Most of our steel is made by this process.

FIG. 291. The brilliant flame of a Bessemer converter

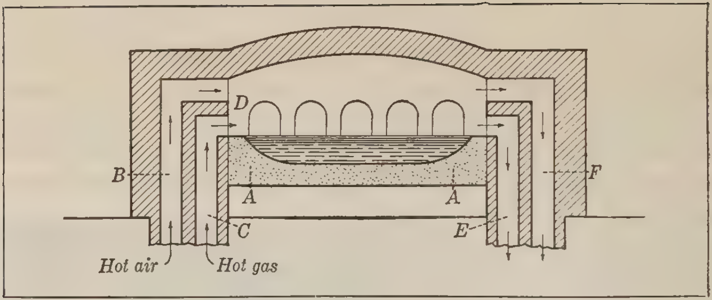


FIG. 292. Diagram of an open-hearth furnace

The fuel gas previously heated enters through *C*, and at *D* meets a current of hot air entering through *B*. The hot flame passes over the cast iron in the furnace, melting it and changing it into steel. The hot products of combustion escape through *E* and *F* and are used in heating the incoming supplies of gas and air. The limestone lining is shown at *A*, *A*

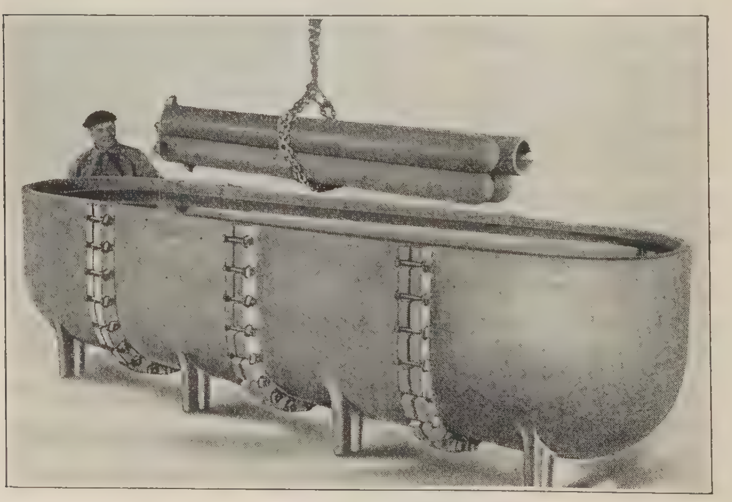


FIG. 293. Cleaning the surface of iron pipes

In the figure there are shown a number of iron objects about to be lowered into a bath of sulfuric acid in order to clean the surface of the iron, since this element, as well as its oxides, is readily attacked by the acid. The bath containing the sulfuric acid is also made of iron, but along with the iron is a certain amount of silicon, these two elements forming an alloy called duriron which is only very slightly attacked by acids

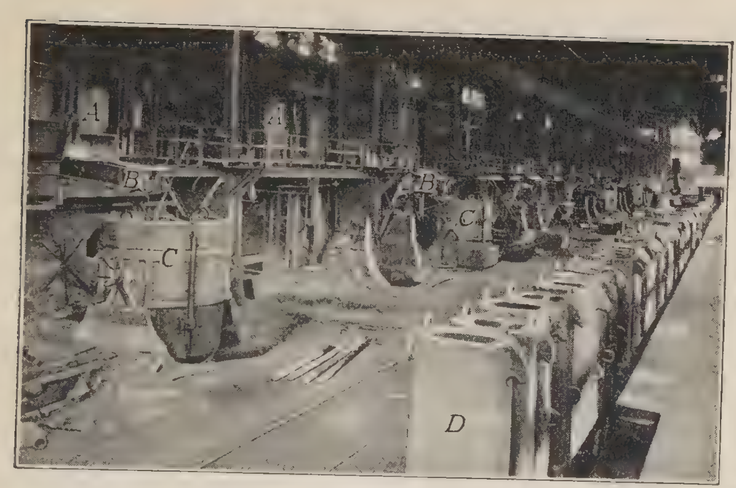


FIG. 294. Casting open-hearth steel

The molten steel flows from the furnaces *A*, *A*, down the troughs *B*, *B*, into the buckets *C*, *C*. It is then poured into the molds *D*, where it solidifies. The blocks of steel so obtained are known as ingots

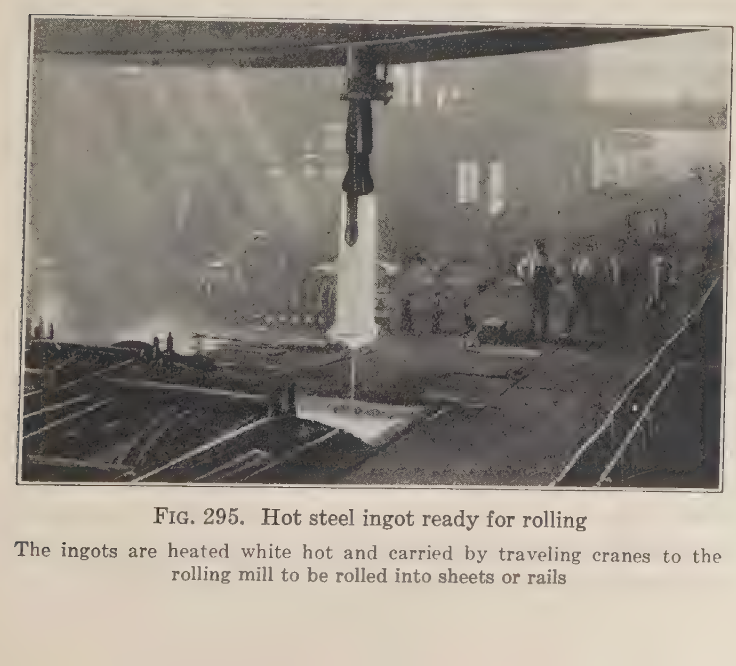


FIG. 295. Hot steel ingot ready for rolling

The ingots are heated white hot and carried by traveling cranes to the rolling mill to be rolled into sheets or rails

637. Electrothermal metallurgy of steel. An increasing quantity of high-grade tool steel is being produced in electrical furnaces. The process is not electrolytic, the electrical current being used merely to produce heat. This method is almost identical with the open-hearth method, save in the way in which the heat is supplied, and produces the same kind of steel as does the latter method, but in smaller lots for special purposes.

638. Properties of steel. Steel contains from a trace up to 2 per cent of carbon, less than 0.1 per cent of silicon, and not more than traces of phosphorus and sulfur. When desired, a product containing as high as 99.85 per cent of iron can be produced by the open-hearth method. Such steel is very soft, but resists rusting. As the percentage of carbon increases, the steel becomes harder and less ductile. Steel can be rolled into sheets, cast in molds, and forged into desired shapes. The world's annual production of steel is more than 100,000,000 tons, of which the United States produces about half.

639. The hardening and tempering of steel. When steel containing from 0.5 to 1.5 per cent of carbon is heated to a relatively high temperature and then cooled suddenly by plunging it into cold water or oil, it becomes very hard and brittle. When gradually reheated and then allowed to cool slowly, this hardened steel becomes softer and less brittle, and this process is known as *tempering.*

By properly regulating the temperature to which the steel is reheated in tempering, it is possible to obtain any condition of hardness demanded for a given purpose, as for making springs or cutting-tools. The surface of steel assumes different colors at different temperatures, and by these the experienced workman can tell when the desired temperature has been reached. Lake gives the following temperatures for the tempering of tools specified:

TEMPERATURES SUITABLE FOR TEMPERING TOOLS

220°	paper cutters, wood-engraving tools
240°	knife-blades, rock drills
260°	hand-plane cutters
275°	axes, springs
290°	needles, screw drivers
300°	wood saws

640. Steel alloys. To secure steel alloys with properties adapted to special requirements, suitable percentages of various elements are added to the melted steel, such as silicon, manganese, nickel, cobalt, chromium, tungsten, vanadium, and titanium. Most of these metals are very difficult to prepare in pure form, so they are not added to the liquid steel in this state. Their oxides are mixed with an iron oxide and with carbon, and the mixture is heated to a high temperature, usually in an electric furnace. The reduced metals form a high-percentage alloy, known by such names as *ferromanganese* and *ferrochromium*. The requisite weight of these alloys is added to the liquid steel to give the resulting alloy the desired composition. A great variety of these alloys are in use, most of them having special trade names.

In general, small percentages of chromium, manganese, nickel, or cobalt give great hardness to steel, suited to armor plate, projectiles, safes, jaw crushers, and the like. Tungsten and molybdenum make a very hard steel alloy that retains its temper at red heat and is suited to high-speed lathe tools. Vanadium steel is very strong and tough, suitable for automobile parts. Many alloys of higher percentages have special trade names. *Duriron* is an alloy containing from 12 to 15 per cent silicon which resists acid corrosion (Fig. 293). *Stainless steel,* containing from 11 to 13 per cent chromium and 0.3 to 0.4 per cent carbon, is used for knife-blades; with larger chromium content up to 30 per cent it is used for acid-resisting purposes. *Staybright* steel is a more recent stainless steel with 18 per cent chromium and 8 per cent nickel.

641. Compounds of iron. Iron differs from the metals so far studied in that its atoms can lose *either two or three* valence electrons, forming the ions Fe^{++} and Fe^{+++}. Consequently we have *two series* of iron salts. In one the iron is *bivalent,* and these salts, both in formulas and in many chemical properties, are similar to the corresponding zinc salts. These are called *ferrous* salts. In the other series iron is *trivalent,* and forms salts similar to those of aluminum. These are known as *ferric* salts.

Most of the metals that remain to be studied have, like iron, at least two valences, and it is evident that such metals form many more salts than those having a single valence. Only a very few can be even mentioned.

642. Ferrous salts. These salts are obtained by dissolving iron in the appropriate acid; or they may be prepared by precipitation if they are insoluble. The crystallized salts are usually hydrates, and light green in color.

Ferrous sulfate ($FeSO_4$). Ferrous sulfate is the most familiar ferrous compound. It is usually obtained in the form of the hydrate, $FeSO_4 \cdot 7\,H_2O$, called *copperas* or *green vitriol,* and is prepared commercially as a by-product in the steel-plate mills. Preparatory to galvanizing or tinning (§ 591), steel plates are cleaned from rust by immersing them in dilute sulfuric acid, and in the process some of the iron dissolves (Fig. 293). The liquors are concentrated, and the green vitriol separates from them. The salt is used in the manufacture of ink, blue pigments, and iron alum, and in the purification of water.

Ferrous sulfide (FeS). This occurs in nature as the yellowish-brown mineral *pyrrhotite.* It is a by-product in certain industries (§ 399), and is also made by heating iron and sulfur together for use in making hydrogen sulfide.

643. Ferric salts. The crystallized, hydrated ferric salts are usually yellow or violet in color. Heated in solution in the absence of free acid, they hydrolyze even more readily than the salts of aluminum. The most familiar ferric salt is the chloride.

Ferric chloride **($FeCl_3$).** This salt can be obtained most conveniently by dissolving iron in hydrochloric acid and then passing chlorine into the solution:

$$\mathrm{Fe} + 2\,\mathrm{HCl} \longrightarrow \mathrm{FeCl_2} + \mathrm{H_2}$$
$$2\,\mathrm{FeCl_2} + \mathrm{Cl_2} \longrightarrow 2\,\mathrm{FeCl_3}$$

A more general way, which can be used in preparing all ferric salts, is to treat an *acid solution* of the ferrous salt with an oxidizing agent:

$$2\,\mathrm{FeCl_2} + 2\,\mathrm{HCl} + \mathrm{O} \longrightarrow 2\,\mathrm{FeCl_3} + \mathrm{H_2O}$$

Ferric sulfate **($Fe_2(SO_4)_3$).** Ferric sulfate is prepared from ferrous sulfate by the use of an oxidizing agent:

$$2\,\mathrm{FeSO_4} + \mathrm{H_2SO_4} + \mathrm{O} \longrightarrow \mathrm{Fe_2(SO_4)_3} + \mathrm{H_2O}$$

Like aluminum sulfate, it forms a series of alums.

644. Oxidation of ferrous salts. If we write the equations for the two methods of preparing ferric chloride in ionic form, we shall have

$$2\,(\mathrm{Fe^{++}}, \mathrm{Cl^-}, \mathrm{Cl^-}) + \mathrm{Cl_2} \longrightarrow 2\,(\mathrm{Fe^{+++}}, \mathrm{Cl^-}, \mathrm{Cl^-}, \mathrm{Cl^-}) \quad (1)$$

$$2\,(\mathrm{Fe^{++}}, \mathrm{Cl^-}, \mathrm{Cl^-}) + 2\,(\mathrm{H^+}, \mathrm{Cl^-}) + \mathrm{O} \longrightarrow 2\,(\mathrm{Fe^{+++}}, \mathrm{Cl^-}, \mathrm{Cl^-}, \mathrm{Cl^-}) + \mathrm{H_2O} \quad (2)$$

It will be seen that in both reactions, whether oxygen is used or not, each ferrous ion (bivalent) loses one more electron and becomes a ferric ion (trivalent). In the first equation chlorine *atoms* capture the electrons lost by the ferrous ions, and become chlorine *ions*; in the second equation hydrogen *ions* capture the lost electrons, become hydrogen *atoms*, and then unite with oxygen to form water. So far as the iron ions are concerned, the two reactions are the same, and the iron is said to be *oxidized*.

Whether oxygen is used in a reaction or not, *the loss of an electron by a metal ion (increase in its valence) is called oxidation.* In both of these reactions, ferrous ions are *oxidized* to ferric ions.

645. Reduction of ferric salts. Ferric salts may be changed into ferrous salts by the action of nascent hydrogen (or other reducing agents) as shown in the following equation:

$$Fe^{+++}, Cl^-, Cl^-, Cl^- + H \longrightarrow Fe^{++}, Cl^-, Cl^- + H^+, Cl^-$$

In this reaction the ferric ion, Fe^{+++}, recovers an electron and is changed into ferrous ion, Fe^{++}. Although no oxygen has been removed, the ferric ion is said to be *reduced* to ferrous ion, while the atom of hydrogen loses an electron and is *oxidized.*

The capture of electrons by a metal ion (decrease in its valence) is called reduction.

646. Oxidation and reduction of anions. Sometimes, though not so often, it is the *anion radical* of a salt that changes its valence rather than the metal cation. When such changes do occur we call them oxidations and reductions. When an anion captures additional electrons it is said to be *reduced*; when it loses electrons it is oxidized.

When hydrogen combines with chlorine to form hydrochloric acid, the atoms of hydrogen (cations) lose electrons and are oxidized; the atoms of chlorine gain electrons (are reduced) to form Cl^- ions.

647. Hydroxides and oxides of iron. A soluble base ($NaOH$) added to a solution of a ferrous salt produces a white precipitate of insoluble *ferrous hydroxide* ($Fe(OH)_2$). This is very rapidly oxidized by air and water to ferric hydroxide.

Ferric hydroxide ($Fe(OH)_3$) is at once precipitated as a rusty-red colloidal substance when a soluble base is added to a solution of a ferric salt:

$$FeCl_3 + 3\ NaOH \longrightarrow Fe(OH)_3 + 3\ NaCl$$

When heated, ferric hydroxide loses water and is converted into *ferric oxide* (Fe_2O_3). This is by far the most important oxide of iron, and occurs in large quantities in nature as hematite. *Magnetic oxide* of iron has the formula Fe_3O_4.

648. Rusting of iron. When exposed to water, ordinary iron changes into reddish-brown rust, which has the composition of the mineral limonite ($2\ Fe_2O_3 \cdot 3\ H_2O$). The iron is first *oxidized* by water (or by carbonic acid) to a ferrous compound, the hydrogen of water being reduced to free hydrogen:

$$Fe + 2\ H_2O \longrightarrow Fe^{++}(OH^-)_2 + H_2$$

The ferrous hydroxide is then oxidized by air to form rust:

$$4\ Fe(OH)_2 + O_2 \longrightarrow 2\ Fe_2O_3 \cdot 3\ H_2O + H_2O$$

Rust is porous, so the action of water is not confined to the surface of the iron. Very pure iron rusts slowly, but alloy material in the iron often hastens rusting.

649. Iron disulfide (pyrite) (FeS_2). This compound occurs very abundantly in nature as brass-yellow crystals, often called *fool's gold.* When pyrite is burned the sulfur is oxidized to sulfur dioxide, and the mineral is often used as a source of sulfur dioxide in making sulfuric acid.

650. Sodium ferrocyanide ($Na_4Fe(CN)_6$); potassium ferrocyanide ($K_4Fe(CN)_6$). These are the sodium and the potassium salts of the acid $H_4Fe(CN)_6$, and are prepared from the by-products obtained in the manufacture of coal gas. They are soluble yellow solids, and the potassium salt is often called *yellow prussiate of potash.* When a solution of either is added to a solution of a *ferric* salt such as ferric chloride, a deep-blue precipitate of ferric ferrocyanide forms. This is called *Prussian blue.* It is used as a paint pigment and sometimes for bluing laundry water. The formation of this blue precipitate is a good test for Fe^{+++} ions.

651. Potassium ferricyanide ($K_3Fe(CN)_6$). By treating a solution of potassium ferrocyanide with chlorine water and evaporating the solution to crystallization, garnet-red crystals are deposited which have the composition $K_3Fe(CN)_6$:

$$2\ K_4Fe(CN)_6 + Cl_2 \longrightarrow 2\ K_3Fe(CN)_6 + 2\ KCl$$

This compound is called *potassium ferricyanide* or *red prussiate of potash.*

When a solution of ferricyanide is added to a solution of a *ferrous* salt a blue precipitate (Turnbull's blue) is formed, which is a good test for Fe^{++} ions.

652. Blue-printing. When a ferric salt and potassium ferricyanide are brought together in solution, no precipitate forms, though the solution acquires a yellowish color. On exposure to the sunlight the ferric salt undergoes a partial reduction to ferrous salt, and a blue precipitate forms. Advantage is taken of these facts in the process of *blue-printing.* A sensitive paper is prepared by soaking paper in a solution of potassium ferricyanide and a ferric salt (ferric ammonium citrate is generally used), and drying it in a dark place. When a black drawing on tracing cloth is placed upon such a sensitive paper and the two are exposed to the sunlight, the sensitive paper (except where it is protected by the black lines) turns a brownish color. It is then thoroughly washed with water to remove the soluble salts, during which process the portions acted upon by the light turn blue, while the unaffected portions are left white. A solution of sodium hydroxide can be used as an ink for white lettering on a blue-print, since this base decolorizes the blue compound present.

Cobalt and Nickel

653. Occurrence. Cobalt and nickel are almost always found together in ores which also contain iron, silver, and copper in combination with arsenic and sulfur. The richest deposits of cobalt are in Ontario, Canada. Nickel is also a frequent impurity of crude copper, and several million pounds of nickel sulfate are annually recovered in the United States in the refining of copper by electrolysis.

654. Properties and uses. Both these metals are silvery in appearance and take a high polish. They are somewhat heavier than iron and melt at a lower temperature. Their chief use is in making alloys. *Nickel steel is of the greatest importance* and is widely used when hardness and resistance to vibration are necessary, as in the construction of parts of machinery, automobiles, locomotives, projectiles, and armor plate. An alloy of cobalt, chromium, and tungsten (trade name, *stellite*) is used for making cutlery and high-speed lathe tools. An alloy of cobalt with tungsten carbide, called by the trade name *carboloy,* is even harder and less damaged by heat than stellite. It is used for lathe tools (Fig. 296), and will even turn glass rods and cut threads on them. *Nickel coinage* consists of three quarters copper and one quarter nickel, while *monel metal,* used so largely because it resists corrosion, is also composed of nickel (3 parts) and copper (1 part). Nickel is also used as a plating upon other metals to prevent corrosion (nickel-plating).

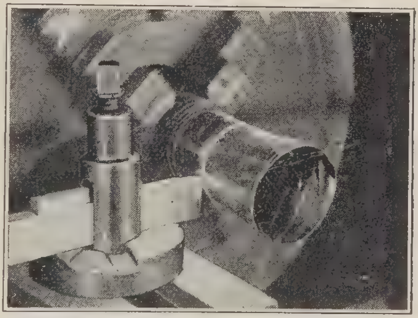


FIG. 296. Carboloy

Cutting a glass tube with a carboloy lathe tool

655. Electroplating with nickel. Nickel-plating is accomplished by an electrolytic process. The object to be plated is suspended in a solution of a nickel salt and serves as the cathode, while a plate of nickel is used as the anode. When the current is passing through the electrolyte the nickel is deposited in the form of a silver-like coating upon the object to be plated, and an equivalent portion of nickel dissolves from the anode, the composition of the electrolyte remaining unchanged. Fig. 297 illustrates the process on a large scale, the objects to be plated being suspended from the rods *C*, *C*.

656. Cobalt oxide (CoO). This is the form in which most of the cobalt comes into the market. It is a black powder used in making other cobalt compounds and in making blue glass and blue decorations on china. Sometimes powdered cobalt glass, called *smalt*, is used instead of the oxide and as a pigment.

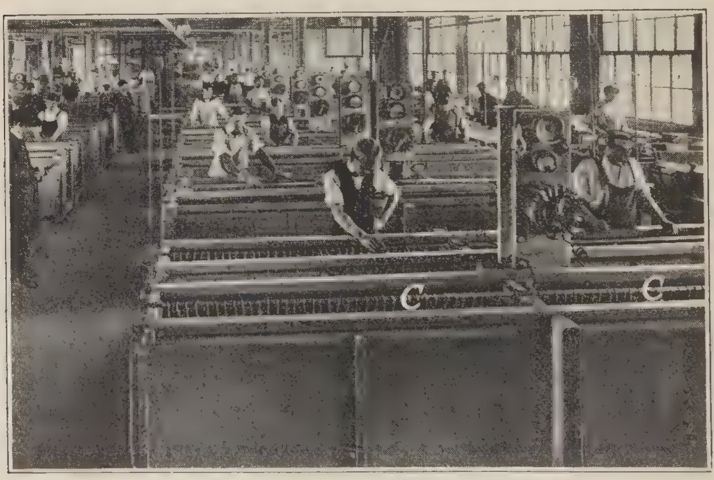


FIG. 297. The process of electroplating with nickel as carried out in a large factory

657. Salts of cobalt and nickel. Nearly all the simple salts of cobalt and of nickel have formulas similar to those of *ferrous* salts. The most familiar are the following:

$Co(NO_3)_2 \cdot 6\,H_2O$	a cherry-red deliquescent salt
$NiSO_4 \cdot 7\,H_2O$	well-formed green crystals

Inks

658. Composition. Inks were known as early as 2500 B.C. and were used in writing. They were black and, like modern india ink, owed their color to carbon. The composition of ordinary black ink may be seen from the following formula, recommended by the United States government: tannic acid, 23.4 g.; gallic acid, 7.7 g.; ferrous sulfate, 30 g.; dilute hydrochloric acid, 25 g.; carbolic acid (phenol), 1 g.; suitable blue dye, 2.2 g.; sufficient water to make 1000 cc.

Tannic acid and the closely related compound, gallic acid, are obtained from the bark of various trees and especially from nutgalls (abnormal growths produced on parts of trees that have been stung by certain insects). *Ferrous salts* do not form a color with tannic and gallic acids, but *ferric salts* produce a black tannate and gallate of iron. When the ink is used the ferrous salt is oxidized by the air to a ferric salt, and this then forms the black iron compound. The dye called for in the formula is used to give a temporary color until the permanent color develops. The acid is necessary to keep the iron in solution. The carbolic acid acts as a preservative to keep the ink from molding. Circular No. 95, issued by the United States Bureau of Standards, gives interesting information concerning inks.

659. Removal of ink and other stains from textiles. Some stains can be removed by simply washing the fabric with the appropriate solvent. Sirup stains, for example, can be removed by washing with hot water. Fruit stains and coffee stains can usually be washed out with boiling water. Since oils and fats are soluble in benzine and carbon tetrachloride, either of these solvents may be used in removing grease spots. Turpentine is a good solvent for fresh paint.

In some cases the stain can only be removed by the action of a reagent that will convert the stain substance into a soluble compound which can then be washed out with water. Thus a dilute solution of oxalic acid is effective in removing ordinary black ink stains, since the acid reduces the ferric salts in the ink to soluble ferrous salts which can then be washed out with water. In other cases the stain substance may be converted into colorless compounds by a mild bleaching agent such as a dilute solution of sodium hypochlorite (the Javelle water of the druggist). In all such cases a test should first be made upon a small clipping of the textile to make sure that the substance used does not harm the textile. It is almost impossible to remove stains from silk because this textile is so sensitive to the action of solvents and reagents.

The whole subject of removal of stains from textiles is discussed in detail in Farmers' Bulletin 1474, published by the United States Department of Agriculture.

CHAPTER SUMMARY IN QUESTION FORM

1. Iron does not commonly occur free in nature, yet it has been familiar for more than four thousand years. Account for the fact that it has been known so long.

2. In what form does iron occur (*a*) in the earth's crust? (*b*) in the human body?

3. (*a*) Name three well-known forms of commercial iron. (*b*) What one element is present in all these forms in addition to the iron?

4. Answer the following in reference to the metallurgy of iron: (*a*) give the size and shape of the furnace in which the ores are reduced; (*b*) name four substances that enter the furnace, and state where each enters; (*c*) give the purpose served by each; (*d*) name three products that leave the furnace, and state where each leaves.

5. Name four elements whose removal from cast iron, wholly or in part, tends to improve the iron for commercial purposes.

6. Prepare on a separate sheet of paper a table that summarizes the facts about the chief varieties of iron as follows:

VARIETY	NAME OF FURNACE USED	MATERIALS ADDED TO FURNACE	PROPERTIES IN RELATION TO CARBON CONTENT, HARDNESS, ABILITY TO HOLD CUTTING EDGE OR TO BE WELDED, CAST, AND TEMPERED	USES
1. Cast iron . .				
2. Wrought iron				
3. Bessemer steel				
4. Open-hearth steel . . .				

7. Name the elements that are used in various steel alloys.

8. What element or elements are added to iron to make it (*a*) very hard? (*b*) able to retain its cutting edge when hot? (*c*) able to resist acid corrosion? (*d*) stainless?

9. Prepare a table of information concerning five important compounds of iron as follows:

FORMULA	COMMON NAME	COLOR	PHYSICAL STATE	USES
1.				
2.				
3.				
4.				
5.				

10. How is it possible to have two series of iron salts, while aluminum forms but one?

11. Show by an equation written in the ionic form (*a*) how the ion Fe^{++} can lose an additional electron and become the ion Fe^{+++}; (*b*) how the ion Fe^{+++} can capture an electron and be changed to the ion Fe^{++}.

12. From the standpoint of the modern theory of the atom, explain the meaning of the words (*a*) oxidation and (*b*) reduction.

13. Explain why iron rusts more rapidly in *moist* air than in dry.

14. Give the composition of (*a*) nickel steel; (*b*) stellite; (*c*) nickel coin; (*d*) German silver.

15. Explain how metal objects are electroplated with nickel.

16. Prepare a table of two columns, in one of which is listed the various stains and in the other the method of removal.

THOUGHT QUESTIONS

1. (*a*) What is the difference between the basic open-hearth process and the Bessemer process? (*b*) Why is most of our steel today made by the open-hearth process rather than the Bessemer?

2. Suggest a reason why none of the metals so far studied occur free in nature.

3. Give the common names of the ordinary hydrates of the sulfates of the following metals: (*a*) sodium, (*b*) magnesium, (*c*) iron (ferrous).

4. Contrast the relative advantages of iron and aluminum as materials for making cooking utensils.

5. What precautions must be taken in removing stains with gasoline?

6. Suppose you had a supply of pure iron and wished to prepare from it the following compounds. Write the equations showing the reactions you would use in the preparation of each: (*a*) ferrous sulfate; (*b*) ferric chloride; (*c*) ferrous sulfide; (*d*) ferric hydroxide.

7. Is there any relation between nickel-plated objects and galvanized iron?

8. Which of the ores of iron listed in § 628 contains the greatest percentage of iron?

9. What weight of iron would be required to make 500 lb. of copperas?

FOR HONOR STUDENTS

1. Collect such objects as a nail, a bolt, a piece of watch-spring, a needle, a knife-blade, the base of a ring stand, a permanent magnet, an electromagnet, a chisel. Label each appropriately as cast iron, wrought iron, soft steel, or hard steel, and display them to the class.

2. Read Chapter XI (entitled "The Chemistry of Inks") in Volume II of "Chemistry in Industry," and write a theme on the subject.

CHAPTER XLII

COPPER, MERCURY, AND SILVER; PHOTOGRAPHY

660. The family. Although mercury is not in the same family with copper and silver, the three elements resemble each other so closely in chemical conduct that it is convenient to class them together for study. The chief ores of all three are *sulfides,* so their metallurgy is different from that of metals whose ores are oxides. These metals are below hydrogen in the displacement series, so they are not acted on by water, or by dilute acids unless oxygen is present.

Copper

The Great Electrical Metal

661. General. When we remember that copper wire is a necessity for winding the armatures of all electrical motors and dynamos; for long-distance telephone, power, and cable lines; for the high-tension coils of the radio, and the starting and ignition systems of automobiles; and that pure copper makes the electrotype plates from which our books are printed and is a necessary component of brass, bronze, all our coinage, most of our jewelry and silver plate, — then we begin to realize how important this metal is in transportation, communication, power, light, and in many of the luxuries and adornments of life.

662. Properties and occurrence. Metallic copper has been known from the earliest times and was the first metal to come into considerable use (Fig. 298). Its use in the making of weapons of war preceded the use of iron. This early use of the metal is due to the fact that relatively large quantities of it are found in a free state, and in this condition it is easily hammered into useful vessels. Its ruddy color also gave it value as an ornament. It is a little heavier than iron, but melts at a lower temperature (1083°). It is rather soft and very malleable, pliable, and ductile (Fig. 299), yet it is tough and strong. As a conductor of heat and electricity it is second only to silver. A few tenths of 1 per cent of certain impurities, notably arsenic, greatly increase its electrical resistance.

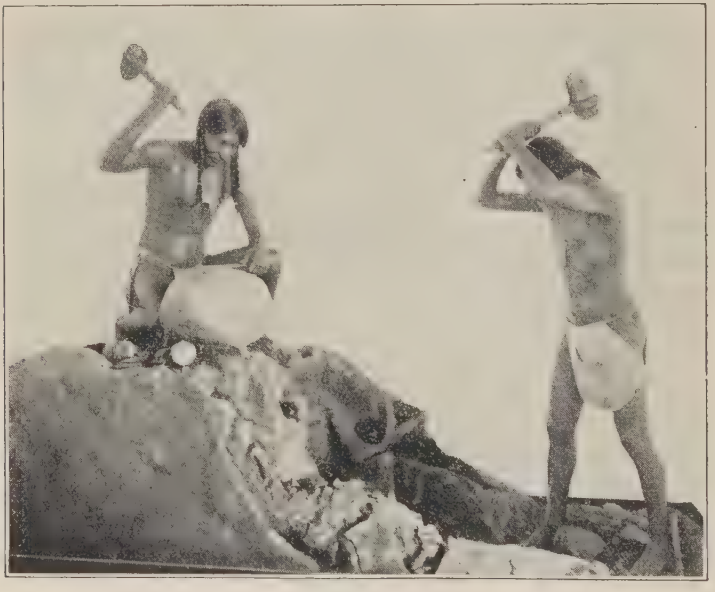


FIG. 298. Mining copper before iron was used

By courtesy of the United States National Museum

Copper occurs native in northern Michigan, while its ores are most abundant in Arizona, Montana, Utah, and Michigan. The most valuable ores are the following:

Chalcopyrite	$CuFeS_2$	Cuprite	Cu_2O
Chalcocite	Cu_2S	Bornite	Cu_3FeS_3

Nearly all civilized countries produce some copper, but the United States produces more than half of the world's supply. Chile is second as a copper-producing country.

663. Metallurgy. The oxide ores are easily reduced with carbon. The metallurgy of the sulfide ores is quite complex and beyond the scope of an elementary text. It need only be said that the copper is first separated in impure form known as *blister copper*, which contains the gold and silver often present in copper ores.

664. Refining of copper. If a pure copper is desired, then the blister copper must be refined by electrolysis. A large plate of it, serving as an anode, is suspended in a tank, facing a thin cathode plate of pure copper. The tank is filled with a solution of copper sulfate and sulfuric acid to act as the electrolyte. An electric current passing through the cell dissolves copper from the anode and deposits it upon the cathode in pure form, while the impurities, including any gold and silver present, collect on the bottom of the tank (Fig. 300). Electrolytic copper is one of the purest of commercial metals.

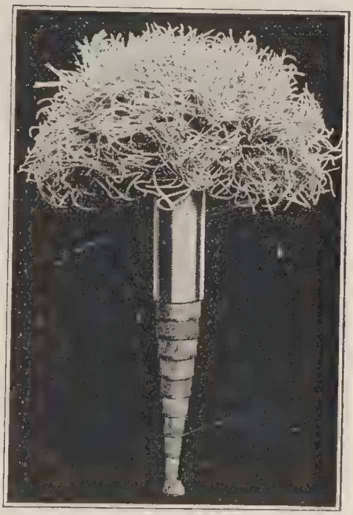


FIG. 299. Fine copper wire

A cable of 1200 pairs of wire frayed out at one end

665. Chemical conduct. Since copper is below hydrogen in the displacement series, hydrochloric acid and dilute sulfuric acid are almost without action upon it; nitric acid and hot concentrated sulfuric acid, however, readily dissolve it (§ 295, 3, and § 347, 3). In moist air it slowly becomes covered with a film of the bright-red oxide Cu_2O, which soon changes to a green carbonate. Heated in the air the metal is easily oxidized to the black oxide CuO.

666. Uses. Copper is extensively used for electrical purposes, for roofs and cornices, for sheathing the bottoms of ships, and for making alloys. A very great variety of copper alloys are made, many of them having special trade names. A few of the most widely used are given in the table.

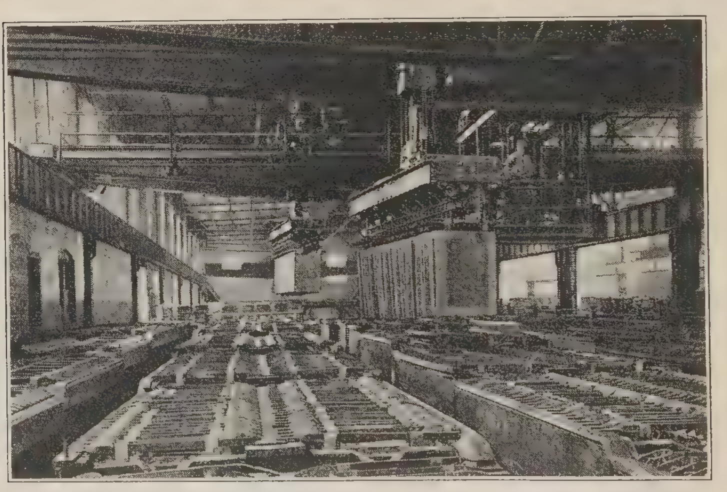


FIG. 300. Refining copper by electrolysis

The figure shows the pure copper cathode raised from an electrolytic cell so that the copper can be removed and the process repeated

COPPER ALLOYS

Brass	60%–90% Cu; 10%–40% Zn
Bronze	80% Cu; 15% Sn; 5% Zn
Aluminum bronze	90% Cu; 10% Al
Manganese bronze	70%–95% Cu; 5%–30% Mn
Monel metal	25% Cu; 75% Ni
Bell metal	78% Cu; 22% Sn
German silver	52%–60% Cu; 25% Zn; 15%–22% Ni
Gold and silver coin	10% Cu; 90% Au or Ag
Nickel coin	75% Cu; 25% Ni

667. Electrotyping. Books are often printed from electrotype plates, which are prepared as follows: Powdered graphite is dusted over a plate of wax, and the face of the type is pressed into this wax by a powerful press. The graphite prevents the wax from sticking to the type, and the pressure packs the graphite into an electrically continuous sheet, coating the impression of the type in the wax. This layer of graphite is now made the cathode in an electrolytic cell containing a copper salt in solution. The copper is deposited as a thin sheet upon the letters in wax, and, when detached, is a perfect copy of the type, the under part of the letters being hollow. The sheet is strengthened by pouring on the under surface a suitable amount of commercial lead. The sheet so strengthened is then used in printing.

668. Two series of copper compounds. Copper, like iron, forms *two series* of compounds: the *cuprous* compounds, in which it is univalent, and the *cupric* compounds, in which it is bivalent. The only important cuprous compound is the oxide Cu_2O, which is a bright-red solid sometimes used to give a ruby color to glass.

669. Cupric compounds. Cupric salts are easily made by dissolving cupric oxide in acids or, when insoluble, by precipitation. In crystallized form most of them are blue or green. Since they are so much more familiar than the cuprous salts, they are frequently called merely copper salts.

***Cupric oxide* (CuO).** This is a black solid obtained by heating copper in excess of air or by igniting the hydroxide or the nitrate. In the laboratory it is used as an oxidizing agent; it is also used for removing sulfur from crude oil in the process of refining.

***Cupric sulfate* ($CuSO_4$).** When crystallized from water, copper sulfate forms large blue crystals of the hydrate $CuSO_4 \cdot 5\,H_2O$, called *blue vitriol* or *bluestone*. The salt is a by-product in silver refining and is also made by the oxidation of pyrite containing copper sulfide:

$$CuS + 2\ O_2 \longrightarrow CuSO_4$$

Blue vitriol is used in electrotyping, in copper refining, and in the manufacture of insecticides. Like all copper salts it is poisonous, especially to lower forms of life. When it is added even in minute quantities to water containing green pond scum (algæ), these plants are quickly killed. The mixture obtained by treating blue vitriol with a cold solution of calcium hydroxide (which precipitates copper hydroxide) is used as a spray for killing germs of fungous diseases on fruit trees; it is called *Bordeaux mixture.*

***Cupric sulfide* (*CuS*).** In the form of a black insoluble precipitate cupric sulfide (CuS) is easily prepared by the action of hydrogen sulfide upon a solution of a copper salt:

$$CuSO_4 + H_2S \longrightarrow \underline{CuS} + H_2SO_4$$

670. Tests for cupric ions (Cu^{++}). Since copper is below iron in the electrochemical series, a bright piece of iron (such as a nail) becomes coated with copper when dipped in a solution of a copper salt:

$$Cu^{++}, SO_4^{--} + Fe \longrightarrow F^{++}e, SO_4^{--} + Cu$$

Ammonia added to a solution of a copper salt produces a deep blue color.

Mercury

The One Liquid Metal

671. Properties and occurrence. Mercury, also called *quicksilver,* stands out prominently among the metals for being the only one that is *liquid at ordinary temperatures.* Its use in thermometers and barometers has made it familiar to everyone. It has long been known and was a favorite with the alchemists. Its most common ore is the sulfide HgS, known as *cinnabar.* This occurs in quantities in

Spain and was mined even as early as Roman times for use as a red pigment. The same sulfide, made in the laboratory by heating mercury and sulfur together, still constitutes a valuable pigment known as *vermilion*. Although a liquid, mercury is much heavier than iron (density 13.546). It boils at 356.9° and freezes at – 38.9°.

672. Metallurgy. Mercury is easily separated from cinnabar. It is only necessary to roast the ore in air. The sulfur burns, leaving the mercury as a vapor, which is then condensed as in ordinary distillation. California, Italy, and Spain lead in the production of the metal.

673. Chemical conduct. When mercury is heated just below its boiling point in the air, it slowly unites with oxygen to form mercuric oxide (HgO); at higher temperatures the oxide decomposes into its elements (§ 39). Toward acids mercury conducts itself very much like copper.

674. Uses. In addition to its use in thermometers and barometers, mercury is used as a liquid over which to collect gases that are soluble in water. It readily combines with metals to form alloys called *amalgams*, and this property is turned to account in extracting gold and silver from their ores. For filling teeth the dentist buys under the name of "amalgam" an alloy of silver with copper, zinc, and tin, which he mixes into a paste with mercury just before using it; the mercury soon forms a solid alloy with the other metals.

Mercury vapor, when cold, does not conduct the electric current. An arc is easily started in a tube containing the *heated* vapor, and a peculiar light fills the tube, rich in green and ultraviolet rays (Fig. 127). Such a tube is known as a Cooper-Hewitt lamp (Fig. 301). If one electrode is iron and the other is mercury, the vapor will conduct the current only in one direction. This mercury vapor lamp is much used as an electrical current rectifier, and as a source of ultraviolet light in the treatment of certain diseases.

675. Compounds of mercury. Like copper, mercury forms two series of compounds illustrated by the chlorides, *mercurous* chloride ($HgCl$) and *mercuric* chloride ($HgCl_2$).

Mercuric oxide (HgO). Mercuric oxide is usually obtained as a brick-red substance by carefully heating the nitrate:

$$2\,Hg(NO_3)_2 \longrightarrow 2\,HgO + 4\,NO_2 + O_2$$

It can also be obtained in a yellow allotropic form.

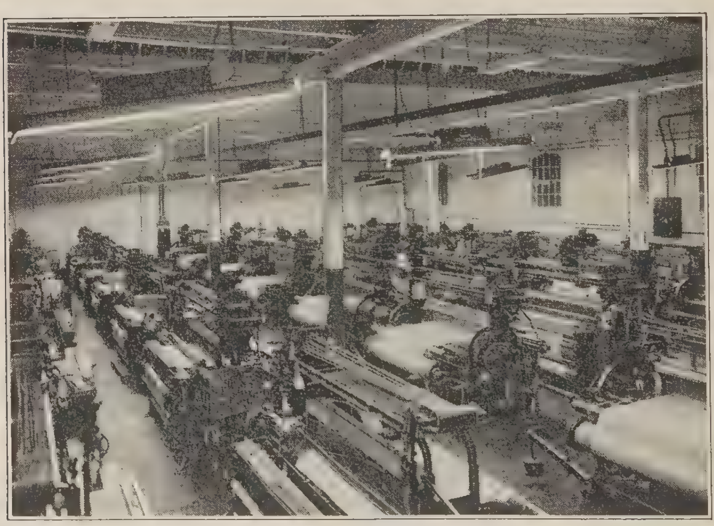


FIG. 301. A factory lighted with Cooper-Hewitt lamps

Mercurous chloride (calomel) ($HgCl$). Being insoluble, mercurous chloride is precipitated as a white solid when a soluble chloride is added to a solution of mercurous nitrate:

$$HgNO_3 + NaCl \longrightarrow \underline{HgCl} + NaNO_3$$

It is the much used medicine called calomel.

Mercuric chloride (corrosive sublimate) ($HgCl_2$). This substance is made on a commercial scale by heating a mixture of common salt and mercuric sulfate:

$$2\,NaCl + HgSO_4 \longrightarrow HgCl_2 + Na_2SO_4$$

The mercuric chloride, being readily volatile, vaporizes and is condensed again in cool vessels. It resembles mercurous chloride in being a white solid, but it is soluble in water. *It is extremely poisonous,* and in dilute solutions is used as an antiseptic in dressing wounds.

Mercuric sulfide (HgS). As *cinnabar,* this substance forms the chief native compound of mercury and occurs in red crystalline masses. By passing hydrogen sulfide into a solution of a mercuric salt, mercuric sulfide is precipitated as a *black* powder insoluble in water and acids. By other means it can be prepared as a brilliant red powder, known as *vermilion,* which is used as a pigment in fine paints.

Silver

The Metal that makes Photography Possible

676. Properties and occurrence. Silver has been known from the earliest times and, together with gold, has always ranked as a precious metal. The Romans called it *argentum* and used it for ornamental purposes and for coins. Like copper, it occurs native as well as in the form of compounds. Most often it occurs in combination with sulfur (Ag_2S) or as a constituent of other sulfides, chiefly those of copper, lead, and arsenic. In the United States it is for the most part produced in connection with lead. Mexico and the United States are the chief silver-producing countries, our center of production being the northern Rocky Mountain states.

Silver is a heavy, rather soft white metal, very ductile and malleable. It is the best conductor of heat and electricity. Its melting point is a little lower than that of copper, and, like gold, it alloys easily with other metals and forms an amalgam with mercury. In the form of a powder it is black.

677. Chemical conduct and uses. Silver is not acted upon by either water or air. Sulfur and its compounds tarnish it, forming black silver sulfide (Ag_2S). Nitric acid is its best solvent, forming silver nitrate ($AgNO_3$). When its compounds are reduced in a glass vessel, the pure metal is deposited as a shining film on the sides of the vessel; hence its use in making *mirrors*. Its use for making tableware, ornaments, and coins is well known. About 150 tons are used annually in making photographic supplies (Fig. 302). Silver coins contain 90 per cent of silver and 10 per cent of copper; *sterling silver* contains 91.6 per cent of silver and 8.4 per cent of copper. The alloy is much harder than pure silver.

FIG. 302. Silver ingots

A week's supply at the kodak factory. The amount of silver used in photography is second only to the government use in coinage

678. Electroplating with silver. Since silver is not acted upon by water or air and has a pleasing appearance, it is used to coat various articles made of cheaper metals. Such articles are said to be *plated*, or, since this word has begun to be applied to other metals also, *silver-plated*, and the process by which this is done is very similar to electroplating with nickel (Fig. 297). The object to be plated (as, for example, a spoon) is attached to a wire and dipped into a solution of a suitable silver salt. This serves as the cathode (Fig. 303), while the anode *A* is made up of one or more plates of silver.

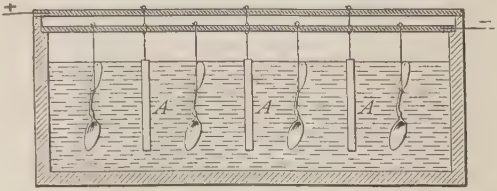


FIG. 303. The process of silver-plating

679. Metallurgy of silver. Because of the great variety of silver ores, many methods of silver metallurgy are employed. In this country the mixed sulfides of silver and lead are reduced together to a silver-lead alloy, and a very ingenious method (known as the *Parkes* method) is then used to separate the silver from the lead.

The alloy is melted and about 2 per cent of zinc is added, which also melts, but most of it does not mix with the alloy, forming a layer on the surface like oil on water. Now at this temperature silver is three thousand times more soluble in zinc than in lead; so if the mixture is stirred the silver nearly all leaves the lead and dissolves in the zinc, rising to the top when the stirring ceases. This layer is skimmed off and distilled, the zinc passing away as vapor and leaving the silver behind to be purified by electrolysis.

680. Compounds of silver. Silver forms only one series of salts, acting as a univalent element in this series.

681. Silver nitrate (lunar caustic) ($AgNO_3$). This salt is a white solid, easily prepared by dissolving silver in nitric acid and evaporating the resulting solution. When cast into sticks it is called *lunar caustic,* for it has a very corrosive action on flesh and is sometimes used in surgery to burn away abnormal growths.

The alchemists designated the metals by the names of the heavenly bodies; for instance, it was they who named quicksilver "mercury." The moon (*luna*) (Fig. 4) was the symbol for silver; hence the name *lunar caustic.*

682. Compounds of silver with the halogen elements. Silver chloride, bromide, and iodide are often known as the *silver halides.* The chloride is white, the bromide pale yellow, and the iodide decidedly yellow. They are insoluble in water and in acids, and therefore are precipitated by mixing a soluble halogen salt with silver nitrate (Fig. 304):

$$AgNO_3 + KCl \longrightarrow \underline{AgCl} + KNO_3$$

These compounds are remarkable for the fact that they are very sensitive to the action of light, undergoing a change of color and chemical composition when exposed to sunlight, especially if in contact with organic matter, such as gelatin. It is upon this property of the silver halides that the art of photography is based.

683. Photography. From a chemical standpoint the processes of photography may be described under two heads: (1) the preparation of the plate for printing, or *negative;* (2) the preparation of the finished picture, or *print.*

FIG. 304. Dissolving silver in nitric acid preparatory to making the silver halides used in photographic films

One company uses six thousand pounds of silver weekly for this purpose

1. ***Preparation of the negative.*** The plate used in the preparation of the negative is made by spreading a thin layer of gelatin, in which colloidal silver bromide is suspended (silver iodide is sometimes added also), over a glass plate or more often a nitrocellulose film (Fig. 305) and allowing it to dry. When the plate so prepared is placed in a camera and the image of some object is focused upon it, the silver salt undergoes a change (not well understood)

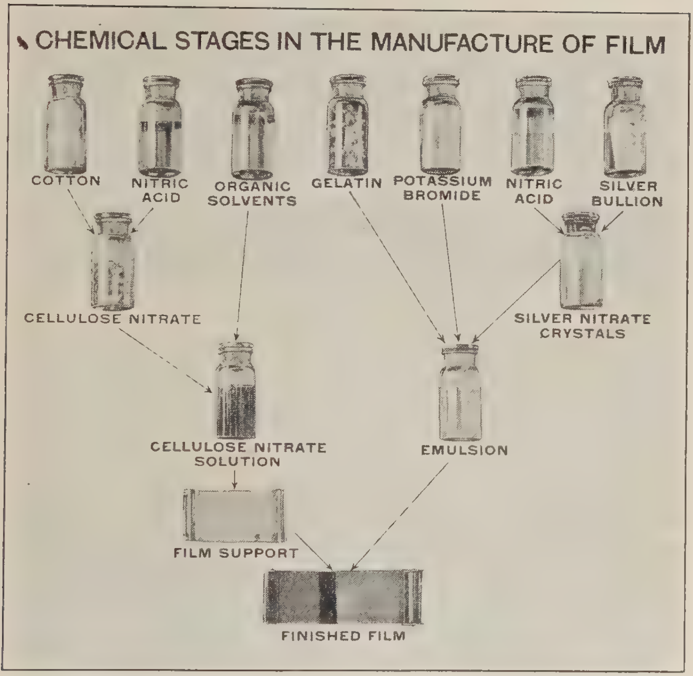

CHEMICAL STAGES IN THE MANUFACTURE OF FILM
COTTON
NITRIC ACID
ORGANIC SOLVENTS
GELATIN
POTASSIUM BROMIDE
NITRIC ACID
SILVER BULLION
CELLULOSE NITRATE
SILVER NITRATE CRYSTALS
CELLULOSE NITRATE SOLUTION
EMULSION
FILM SUPPORT
FINISHED FILM

FIG. 305. Steps in the production of the photographic film

The various raw materials used in the production of the film are shown in the upper row. The cotton (cellulose) and nitric acid react to form cellulose nitrate (§ 494), which is dissolved in a mixture of alcohol and ether to form the cellulose nitrate solution. The silver and nitric acid react to form silver nitrate. This is then mixed with gelatin and potassium bromide. The silver nitrate and potassium bromide react to form silver bromide, which is suspended in the gelatin in the form of an emulsion. The emulsion is then spread over the film support and dried, thus forming the finished film. (Courtesy of the Eastman Kodak Co.)

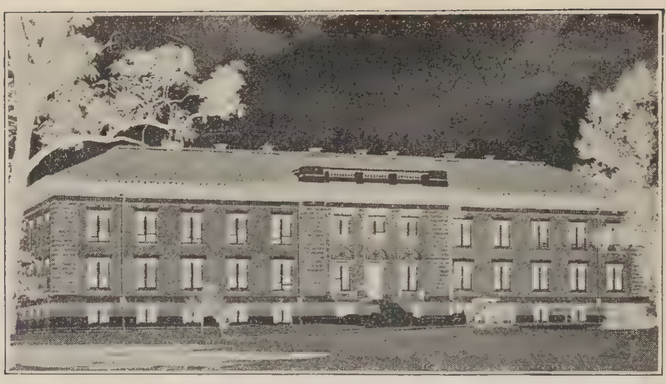


FIG. 306. The negative plate

The photographic plate or film, after exposure in the camera, is immersed in a solution of a reducing agent (the developer) which reduces the silver salt that has been acted upon by the light to black metallic silver. The unaffected silver salt is then dissolved, leaving a picture of the object photographed on the plate, but with the lights and horizontal directions exactly reversed. A plate so prepared is called a *negative*

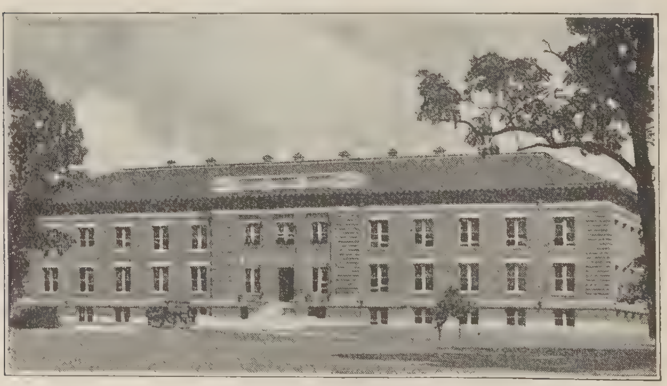


FIG. 307. The positive print

The print is made from the negative. The photographic paper on which the print is to be made is placed under the negative and exposed to the light. The paper is then treated with a developer, and the unaffected silver salts are dissolved off as in the preparation of the negative. Since the darkest places on the negative cut off the most light, the lights of the print will be the reverse of those of the negative; in other words, they will correspond to those of the object photographed which is proportional at each point to the intensity of the light falling upon it. In this way an image of the object photographed is produced upon the plate. This image, however, is invisible and is therefore called *latent*. It can be made visible by the process of *developing*.

To develop the image the exposed plate is immersed in a solution of some reducing agent called the *developer*. While the developer will *in time* reduce all the silver salt, it acts much more rapidly upon that which has been exposed to the light. The action is therefore continued only long enough to bring out the image. The reduced silver is deposited in the form of a black film which sticks closely to the plate.

The unchanged silver salt is now removed from the plate by dipping it in a solution of sodium thiosulfate (*hypo*) (§ 550). The plate is then washed with water and dried. The plate so prepared is called the *negative* (Fig. 306) because it is a picture with the lights and directions exactly reversed.

2. ***Preparation of the print.*** The print is made on paper which is prepared in much the same way as the negative plate. The negative is placed upon this paper and exposed to the light in such a way that the light must pass through the negative before striking the paper. If the paper is coated with silver chloride a visible image is produced, in which case a developer is not needed. *Proofs* are made in this way. In order to make them permanent the unchanged silver chloride must be dissolved off with sodium thiosulfate. The print is then *toned* by dipping it into a solution of gold or platinum salts, in which process the silver on the print passes into solution, while the gold or platinum takes its place. These metals give a characteristic color or tone to the print, the gold making it reddish brown, while the platinum gives it a steel-gray tone. Since the darkest places on the negative cut off the most light, it is evident that the lights of the print (Fig. 307) will be the reverse of those of the negative and will therefore correspond to those of the object photographed.

CHAPTER SUMMARY IN QUESTION FORM

1. Name three uses of copper, each of which is dependent upon a different property.

2. Mention five properties of copper that make it a useful metal.

3. What countries furnish most of our copper?

4. Give the names and composition of two important copper ores.

5. Show by diagram how impure copper is refined.

6. "Copper, like iron, forms two series of compounds." (*a*) How do we distinguish between the two series? (*b*) What is the valence of copper in each? (*c*) Give the name and formula of a compound belonging to each series.

7. Write the equation for the preparation, and state one important use, of (*a*) black copper oxide; (*b*) blue vitriol.

8. In what respect does mercury differ from all other metals?

9. State the properties of mercury that make it adapted (*a*) for use in barometers and thermometers; (*b*) for the manufacture of amalgams; (*c*) for changing an alternating electric current to a direct current.

10. A mercury thermometer could be used for obtaining the temperatures between what limits?

11. Prepare a table of four important compounds of mercury as follows:

FORMULA	COMMON NAME	PHYSICAL STATE	COLOR	ONE USE
1.				
2.				
3.				
4.				

12. State the properties of silver that make it a useful metal.

13. Give the names, formulas, and physical appearance of three important compounds of silver.

14. Illustrate by diagram the method of electroplating with silver.

15. Distinguish between (*a*) pure silver, (*b*) sterling silver, and (*c*) silver-plated articles.

16. (*a*) Give the steps in the preparation of silver chloride from a bar of pure silver. (*b*) Write the equation for the last step in the process, and tell why the reaction goes to completion.

17. Why is silver bromide used in photography?

18. (*a*) What chemical change does silver bromide undergo in the preparation of a negative? (*b*) Why is the negative so called?

19. Why does the sensitiveness of both the photographic plate (or film) and the print cease after they are dipped into a solution of "hypo"?

20. Study the electrochemical series (§ 256) and explain why gold salts are used in *toning* prints, rather than the cheaper copper and tin salts.

THOUGHT QUESTIONS

1. Why should we expect the metals studied in this chapter not to be acted upon by water, nor by acids with the liberation of hydrogen?

2. In electroplating with silver, why use silver in place of some cheaper metal or carbon as an anode?

3. Write the equations for the reactions (if any) that occur when copper is treated with each of the following acids: (*a*) hydrochloric; (*b*) nitric; (*c*) dilute sulfuric; (*d*) concentrated sulfuric.

4. Give two reasons for adding copper to the silver used in silver coins.

5. What is the distinction (*a*) between blue vitriol and green vitriol? (*b*) between copper sulfate and copperas?

6. The alchemists believed that a piece of iron immersed in a solution of blue vitriol is changed into copper. What reason had they for this belief?

7. What undesirable property has nitrocellulose as a material for making photographic films?

8. How could you distinguish (*a*) the oxide of copper, (*b*) the oxide of mercury, (*c*) the oxide of zinc, from each other?

9. Suppose you were given the following substances: sulfuric acid; hydrochloric acid; nitric acid; marble; copper; zinc. What gases could you prepare from these substances?

10. Suppose you got mercury in contact with a gold ring. What would be the result?

11. A silver dollar weighs approximately 26.5 g. What weight of (*a*) silver nitrate and of (*b*) copper nitrate could be prepared from such a coin?

12. A certain company uses 6000 lb. of silver weekly for photographic purposes. How many pounds of silver bromide could be made from this weight of silver?

FOR HONOR STUDENTS

1. Place a new film (4 to 6 exposures) in a camera. (*a*) Take two or three pictures of your schoolhouse or your class, using the proper time-exposure. (*b*) Take another picture of some object in the bright sunlight, using an exposure of one minute. (*c*) Leave the remaining part of the film unexposed. Now subject the film to the process of developing and fixing. Exhibit the resulting film to the class and explain the results obtained in each case.

2. Read Chapter XVIII (entitled "Photography, or Picture Making by Light") in Volume I of "Chemistry in Industry," and write a theme on the subject, or report orally.

CHAPTER XLIII

TIN AND LEAD; PAINTS

684. ***Introduction.*** Everyone is familiar with tin in the form of tin cans and roofing materials, and with lead as lead water-pipes and in bullets and shot, while few people have any acquaintance with compounds of these two metals. This is to be expected; for, aside from the use of lead compounds in paint, tin and lead are used almost wholly either in pure form or in alloys.

Tin

The Protector of Iron

685. Occurrence. In the palmy days of Egypt and Chaldea, the dwellers in a very small country called Phœnicia were the sea-roving merchants of the Mediterranean. More than 1000 years B.C. they knew about the heavy tinstone of what is now Cornwall, and carried the tin from that source to be sold throughout Asia Minor to *harden* copper — that is, to change it into bronze alloy.

Tin is the one important metal with which, so far as we know, nature has failed to endow the United States, and our production of the metal is very small — merely a few tons annually. The world's supply comes chiefly from the Malay States (Fig. 308), the Dutch East Indies (Banka), and Bolivia. Tin is found chiefly as impure oxide, SnO_2, called *tinstone* or *cassiterite*; sometimes as a heavy black sand (stream tin) or in larger masses that are mined.

686. Properties. Pure tin, called *block* tin, is a soft white metal with a silver-like appearance and luster; it melts readily (at 231.8°) and is somewhat lighter than copper. It is malleable and can be rolled out into very thin sheets, forming *tin foil*; most tin foil, however, contains a considerable percentage of lead. When exposed to a low temperature for a long time, tin slowly changes into a gray powder. This transformation, called tin disease (Fig. 309), sometimes destroys tin objects in very cold countries.

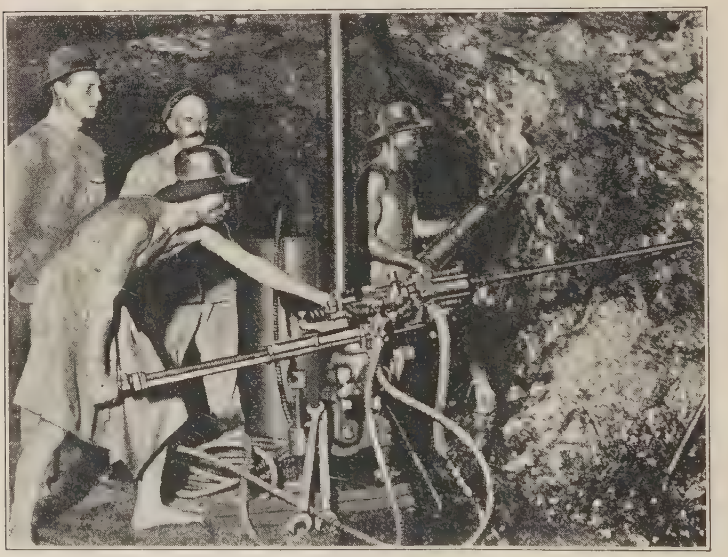


FIG. 308. Mining tin in the Malay States

687. Metallurgy. The metallurgy of tin is very simple, the chief difficulty being in freeing the ores from troublesome impurities before reducing the oxide. It is only necessary to heat the purified ore with coal in a simple reverberatory furnace (Fig. 292):

$$SnO_2 + C \longrightarrow Sn + CO_2$$

688. Chemical conduct. Under ordinary conditions tin is unchanged by air or moisture, but at a high temperature it burns, forming the oxide SnO_2. Dilute acids have little effect upon it, but concentrated acids attack it readily. Concentrated hydrochloric acid slowly changes it into the chloride $SnCl_2$.

689. Uses of tin. A great deal of tin is used in the making of *tin plate.* The process consists in dipping thin sheets of iron (or copper) into the melted tin and is quite similar to that of galvanizing iron (Fig. 271). Owing to its resistance to the action of air and weak acids, tin plate is used in many ways, as in roofing and in the manufacture of tin cans, cooking vessels, and similar articles. Small pipes of block tin are used instead of lead for conveying pure water or liquids containing dilute acids, such as soda water. Many useful alloys contain tin. *Pewter* and *soft solder* are alloys of tin and lead (§ 706).

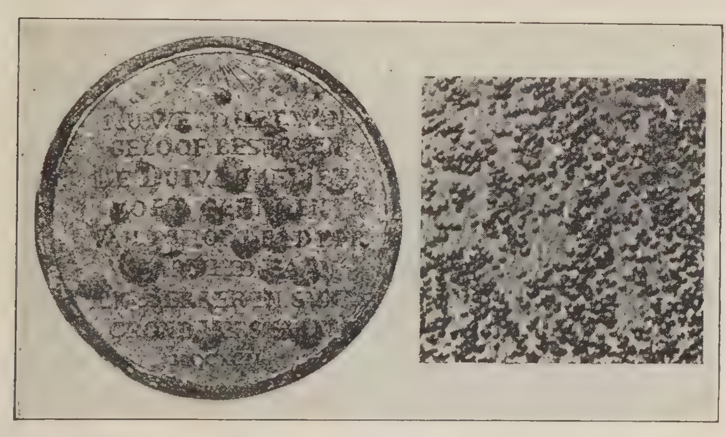


FIG. 309. Tin objects that have been kept at a low temperature for a long time, showing the partial change into the gray powdered form (tin disease)

690. Soldering and brazing. The use of solder in joining two metal surfaces depends upon (1) the low melting point of the solder and (2) the fact that it flows over *clean* metal surfaces and sticks to them on cooling. To secure clean surfaces free from oxide a suitable *flux* must be used which will either *dissolve* the oxide as fast as it forms or will *reduce* it again to metal. The usual fluxes are zinc chloride, ammonium chloride, tin chloride, or material containing one of these. Rosin is sometimes used. In *brazing* or *hard soldering* the process is essentially the same except that a low-melting brass is used instead of solder, and borax is used as a flux.

691. Compounds of tin. Tin forms two series of metallic compounds: the *stannous,* in which the tin is bivalent, as is illustrated in the compounds SnO, SnS, $SnCl_2$, and the *stannic,* in which it is quadrivalent, as appears in the compounds SnO_2, SnS_2, $SnCl_4$. Nearly all tin salts are white.

692. Chlorides of tin. *Stannous* chloride ($SnCl_2$) is prepared by dissolving tin in concentrated hydrochloric acid and evaporating the solution to crystallization. If metallic tin is heated in a current of dry chlorine, *anhydrous stannic* chloride ($SnCl_4$) is obtained as a heavy colorless liquid which fumes strongly on exposure to air. A great deal of tin in the form of stannic chloride is recovered from scrap tin by the action of chlorine. From solution in water a solid hydrate is obtained of the formula $SnCl_4 \cdot 5\,H_2O$.

The chlorides of tin are much used as mordants in dyeing processes, in calico printing, and to give weight to silk.

693. Reducing action of stannous ions. Stannous ions (Sn^{++}) tend to lose two more electrons to become stannic ions (Sn^{++++}). Therefore they are strong *reducing* agents:

$$\begin{aligned} &Hg^{++},\ Cl^-,\ Cl^- + Sn^{++},\ Cl^-,\ Cl^- \\ &\qquad \longrightarrow Hg + Sn^{++++},\ Cl^-,\ Cl^-,\ Cl^-,\ Cl^-, \end{aligned}$$

or

$$Hg^{++} + Sn^{++} \longrightarrow Hg + Sn^{++++}$$

Lead

694. Properties. Articles made of lead have been found in very old Egyptian ruins, and there is no doubt but that it was used from early times. The Romans called it *plumbum* and used it for water pipes, as we do today. It is a heavy metal which has a bright luster on a freshly cut surface but soon tarnishes on exposure to air. It is soft, melts easily, has little strength, and is a poor conductor.

695. Occurrence. The United States produces nearly half of the world's supply of lead, the chief lead-producing states being Missouri, Utah, Idaho, and Oklahoma. The chief ore is *galenite* (PbS) (Fig. 310), and it usually contains some silver and other metals.

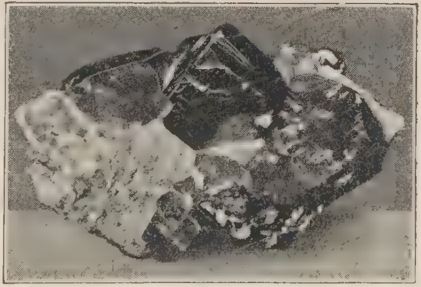


FIG. 310. A crystal of galenite embedded in calcite

696. Metallurgy. Lead is obtained from its ores by a rather complicated process of roasting and reduction. The crude lead first prepared is alloyed with any silver or gold present in the ores, and with varying small percentages of other metals. The impure lead is melted in an open furnace with free access of air. Iron and other easily oxidized impurities are oxidized and, as oxides, float on the heavier lead, from which they can be skimmed off as a scum. Silver and gold remain in the lead and are removed either by the Parkes process (§ 679) or by electrolysis of the lead.

697. Chemical conduct. When lead is heated in the air it forms a yellow oxide (PbO). With the exception of hydrochloric and sulfuric acids (which form insoluble compounds), most acids, even very weak ones, act upon the metal in the presence of dissolved oxygen, forming soluble lead salts. Hot concentrated hydrochloric and sulfuric acids also attack it to a slight extent.

698. Uses. Lead finds many important applications in the industries, chiefly in the manufacture of storage batteries, in linings for sulfuric acid plants, for covering cables of electric wires, in alloys of various kinds (such as shot, antifriction metals, type metal, solder, and pewter), and in water pipes for plumbing. Since lead dissolves to some extent in pure water, it should not be used for pipes that are to carry rain water. *About one third of the annual production of lead is used in making paint* and is permanently lost.

699. Compounds of lead. In nearly all its compounds lead is bivalent, but in a few of its compounds it has a valence of four. All ordinary bivalent lead *salts* are white unless the acid radical has a marked color (for example, lead iodide is scarlet).

All lead compounds are more or less poisonous, and are *cumulative* in their effects. This means that even very small repeated doses accumulate in the system and finally produce lead poisoning. Lead workers of all kinds — those who work with paints, batteries, sheet lead, and the like — must be on the watch for symptoms of such trouble.

700. Lead sulfide (PbS). In nature this compound occurs in a highly crystalline form called *galenite* (Fig. 310), the crystals having much the same color and luster as pure lead. It is readily prepared in the laboratory as a black precipitate, by the action of hydrogen sulfide upon soluble lead salts:

$$Pb(NO_3)_2 + H_2S \longrightarrow \underline{PbS} + 2\ HNO_3$$

701. Lead oxides. Lead forms a number of oxides, the most important of which are the following:

1. ***Litharge*** **(PbO).** This oxide forms when lead is oxidized at about 600° and is obtained as a by-product in silver refining. In color it ranges from yellow and light brown to orange, depending on its mode of production. It is used chiefly in making glazes and flint glass.

2. ***Red lead, or minium*** **(Pb_3O_4).** Minium is prepared by heating lead (or litharge) to about 450° in a current of air. It is a heavy powder of a beautiful red color and is much used as a pigment for painting structural iron, since it protects the metal from rusting. Plumbers use it, mixed with linseed oil, to make gas-tight joints in pipes.

3. ***Lead peroxide*** **(PbO_2).** The peroxide can be prepared as a chocolate-brown powder by oxidizing litharge under proper conditions. It forms the active material on the positive plates of the usual type of storage battery.

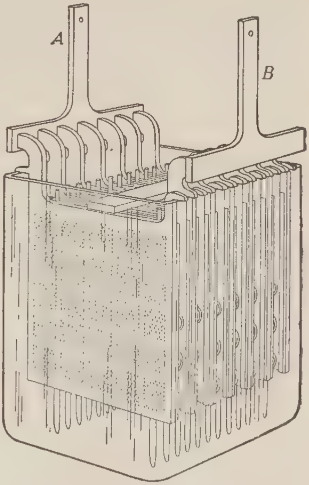


FIG. 311. A seven-plate storage battery

702. Storage battery. In a storage battery (Fig. 311) the negative plates are lead, the positive plates are layers of lead peroxide on a lead support. The electrolyte is dilute sulfuric acid. When the battery is delivering current, the negative plates are being oxidized and the positive lead peroxide plates are being reduced, both forming lead oxide (PbO), which is changed into insoluble lead sulfate on the electrodes, thus withdrawing sulfuric acid from the electrolyte. When the battery is being charged, all these chemical changes are reversed. A test of the density of the electrolyte shows how far the discharging reaction has gone and when the battery needs charging.

703. Lead carbonate. The normal carbonate of lead ($PbCO_3$) is found to some extent in nature and can be prepared in the laboratory; a basic carbonate, however, can be obtained much more easily. This is a compound of lead carbonate and lead hydroxide, $(PbCO_3)_2 \cdot Pb(OH)_2$, and is commonly called *white lead*. It is prepared on a very large scale as a white pigment and as a body for paints which are to be colored with other substances.

704. Manufacture of white lead. White lead can be prepared by a number of processes, but no other seems to produce a product of as desirable physical properties as the old Dutch process, which has been used for centuries, though with many improvements. In this process the lead is cast into perforated plates called *buckles* (Fig. 312, *A*), which are placed loosely upon each other in a crock of the shape shown in Fig. 312, *B*, the ledge formed by the constriction of the crock supporting the plates. The crocks are now placed in rows, one above the other, and separated by layers of tanbark (Fig. 312, *C*). The tanbark slowly ferments, generating carbon dioxide. Sufficient heat is evolved in this process to vaporize the acetic acid. Through the action of the acetic acid and carbon dioxide, the lead is slowly converted into white lead.

705. Other important compounds of lead. In addition to those already described, the most important compounds of lead are as follows:

Lead nitrate ($Pb(NO_3)_2$)	white soluble crystals
Lead chloride ($PbCl_2$)	white needles, soluble in hot, slightly soluble in cold, water
Lead sulfate ($PbSO_4$)	an insoluble white crystalline powder
Lead acetate ($Pb(C_2H_3O_2)_2 \cdot 3\ H_2O$)	a soluble white salt called *sugar of lead* (§ 506)
Lead chromate ($PbCrO_4$)	used as a pigment in paint (*chrome yellow*)

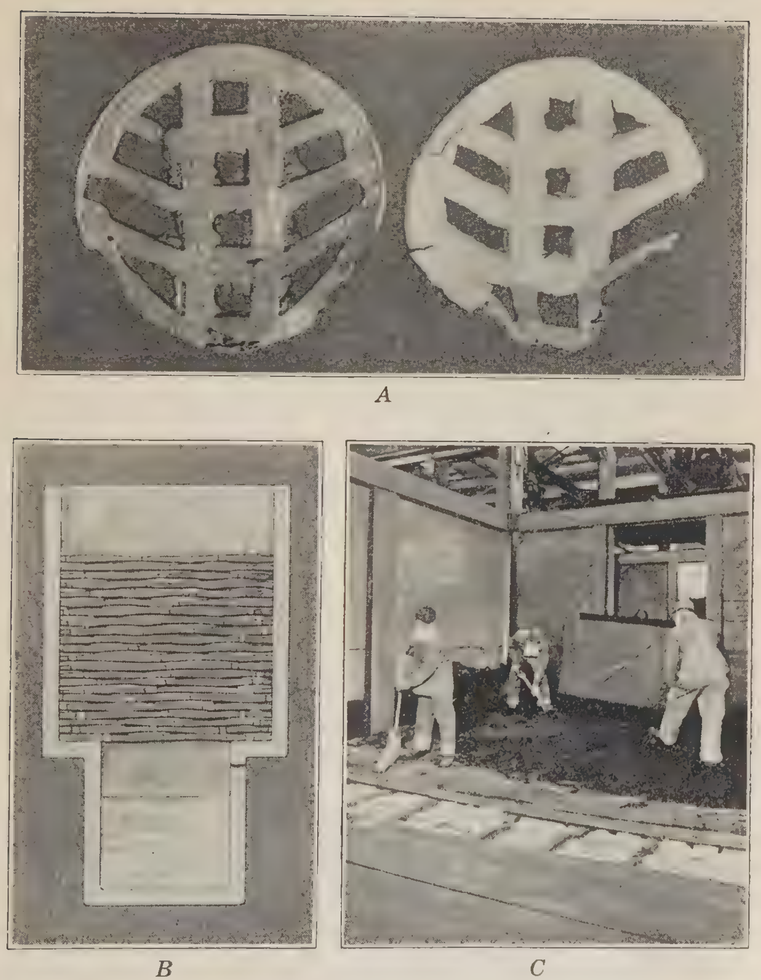


FIG. 312. Steps in making white lead for use in paints

A: Lead plates (buckles) before and after exposure to acetic acid and carbon dioxide. *B*: The lead plates placed in a crock, the lower part of which is filled with acetic acid. *C*: The crocks filled with the lead plates and acetic acid are placed in tiers and covered with spent tanbark (the bark of a tree rich in tannin, such as oak bark). The figure shows the workmen removing the tanbark, after the action is complete. The lead plates, now converted into white lead, are seen where the covering has been removed

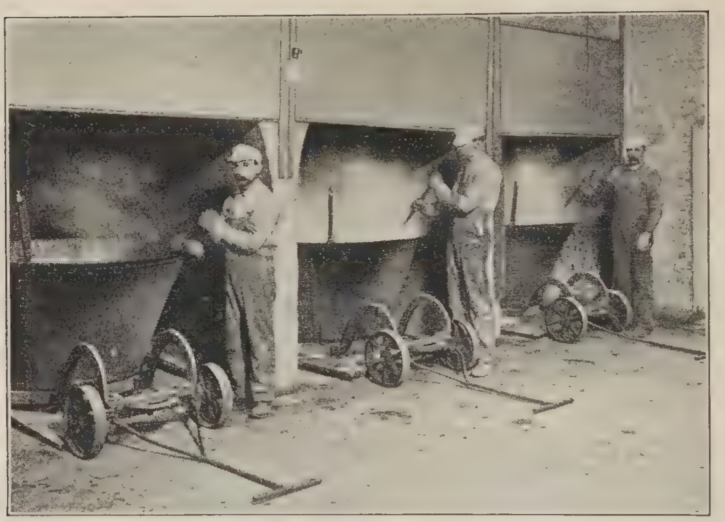


FIG. 313. Making varnish

The resin is placed in large iron kettles set on wheels, and melted over a fire. The kettles are then drawn away from the fire, and the resin is dissolved in linseed oil together with oil of turpentine or a similar liquid, such as benzine

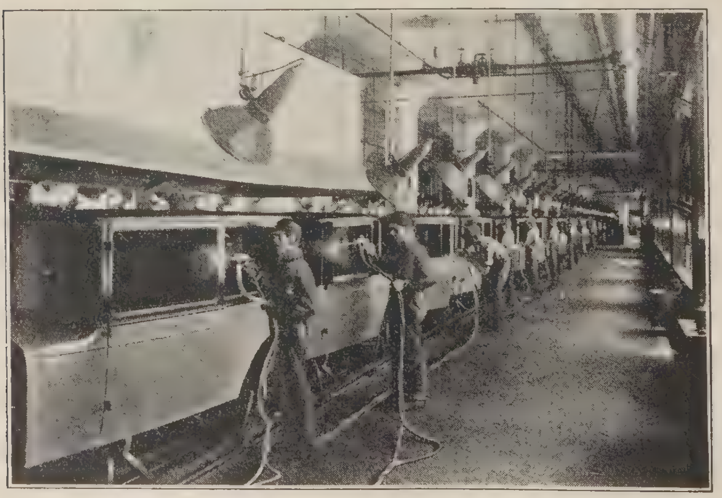


FIG. 314. Spraying automobile bodies with lacquers

706. Some alloys of tin and lead. Some of the important alloys of lead are as follows:

Babbitt	Sn, Sb, Cu	Frary metal	Pb, Ca
Solder	Sn, Pb	Type metal	Pb, Sb, Sn
Pewter	Sn, Pb	Rose metal	Bi, Pb, Sn

Paints

707. Composition. A paint consists of three essential ingredients: the *vehicle*, the *body*, and the *pigment*.

1. ***The vehicle, or liquid medium.*** This must be an oil *which will rapidly oxidize into a more or less flexible, hornlike body.* Such oxidation is called *drying*, and the oil is called a *drying oil.* Linseed oil has long been used as the standard drying oil, since it can be produced in quantity and at moderate cost. Tung oil, a Chinese wood oil, is also used. It is customary to add to it *driers*, made by boiling some of the oil with oxides of manganese, lead, or cobalt. The oxides enter into combination with the oil and assist catalytically in its oxidation. Since people are very reluctant to have wet paint about them, speed in drying is being demanded more and more, and so the tendency is to use increasing quantities of drier.

2. ***The body.*** The body of the paint must be some solid material, suspended in the oil, which will give a smooth and waxy surface as the paint dries and will have good covering power. While white lead meets these requirements, it is moderately expensive, and is blackened by sulfur compounds likely to be present in the air of cities. Other bodies are now frequently combined with the lead or replace it altogether, among them being zinc oxide, barium sulfate, products called by the trade names lithopone (Fig. 269) and titanox, the latter being a mixture of titanium oxide (TiO_2) and barium sulfate. For some purposes these materials are a real advantage, and they are not to be regarded as adulterants unless sold as white lead.

3. ***The pigment, or coloring matter.*** In the case of white paints the body serves also as the coloring matter. For other paints a color pigment must be added. Frequently these pigments are metallic oxides or salts, and in many cases they are natural products. Sometimes they are prepared by precipitating an amorphous (colloidal) body in the presence of an organic dye, the dye being adsorbed by the precipitate (§ 617) and giving it a color. Such pigments can be prepared in an endless variety of colors and are called *lakes*. Usually they are not so permanent as mineral pigments.

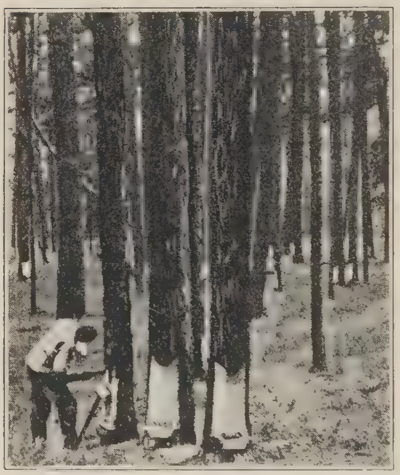


FIG. 315. Making incisions in pine trees

From these incisions exudes a resinous mass, the raw material from which ordinary rosin and oil of turpentine are prepared

708. Varnish. Varnish is a liquid that, on being applied to a surface and then left to stand, forms a closely adhering film that is generally transparent. Varnishes are made by dissolving in appropriate solvents the resins (or gums) obtained from certain trees. There are two chief kinds. In the one the resin is dissolved in linseed oil *thinned* with spirits of turpentine or a similar liquid, such as benzine. On exposure to the air the turpentine evaporates and the linseed oil oxidizes and dries as in paints. In the other class, known as *spirit varnishes*, the resin is dissolved in some volatile liquid, as spirits of turpentine or alcohol. On exposure to air the solvent quickly evaporates, leaving the resin. Spirits of turpentine and rosin (which is not a true resin, but is sometimes used in varnish) are obtained from pine trees, especially from a species that grows in the Southern states (Fig. 315).

709. Lacquers. Lacquers have rapidly displaced varnishes and paints on automobiles, furniture exposed to weather, and for many other uses. They are made of the following: (1) *cellulose nitrate* (§ 494) dissolved in a suitable solvent; (2) *camphor* or some similar material to prevent the cellulose nitrate from cracking when dried; (3) some organic basic compound to neutralize the acids of nitrogen formed by the slow decomposition of the cellulose nitrate; (4) usually *resin* to give hardness and luster to the finished surface; (5) a *pigment* of appropriate color (if color is desired).

On large objects lacquers are applied by spray-guns. They dry so rapidly that an automobile can be sent from the paint shop in two days instead of the two weeks or more formerly required (Fig. 314). They resist weather extremely well.

CHAPTER SUMMARY IN QUESTION FORM

1. (*a*) Give the name and composition of the chief ore of tin, and (*b*) state how the tin is separated from the ore.

2. What are the properties of tin that make it a useful metal?

3. (*a*) What is tin plate? (*b*) To what other product is it similar?

4. What is the composition of (*a*) block tin? (*b*) pewter? (*c*) soft solder?

5. (*a*) What two properties of solder make it possible to join two metal surfaces by its use? (*b*) How does a flux aid in the operation?

6. Tin forms two series of compounds. (*a*) What is the valence of tin in each? (*b*) How do we distinguish between the two in name? (*c*) Illustrate by giving the names and formulas of the two chlorides.

7. What evidence have we that lead has long been known?

8. Name the chief sources of our supply of lead.

9. Prepare a table giving the following information concerning each of the three oxides of lead:

CHEMICAL NAME	COMMON NAME	PHYSICAL STATE	COLOR	USE
1.				
2.				
3.				

10. State the chemical changes taking place when a storage battery is delivering a current.

11. Give the chemical name, the common name, and the composition of a lead compound that is prepared on a large scale for use in making paints.

12. (*a*) Name the three essential ingredients of paint, and (*b*) state the purpose served by each.

13. Name two properties of lacquers that make them useful in the automobile industry.

THOUGHT QUESTIONS

1. Mention three products, each of which is protected by a coating of pure metal.

2. What salts other than those of tin are used as mordants?

3. How is the condition of a storage battery tested? Explain.

4. The air in a chemical laboratory is likely to contain hydrogen sulfide from time to time. Which of the following pigments would be best adapted for painting the walls of such a laboratory: lithopone, zinc oxide, or white lead?

5. What substances obtained from trees are used in the paint industry?

6. What properties in common have benzine, spirits of turpentine, alcohol, and benzene that adapt them for use in the paint industry?

7. Linseed oil is more expensive than cottonseed oil. Why not use the latter in making paint?

8. If a child swallows a poisonous dose of the sweet-tasting sugar of lead (§ 705), a solution of Epsom salts is said to be a good antidote. Explain its action, basing your explanation on the fact that insoluble substances are not absorbed in the system.

9. Give the formula for each of the following: (*a*) cassiterite; (*b*) galenite; (*c*) litharge; (*d*) red lead; (*e*) white lead; (*f*) sugar of lead.

10. Calculate the percentage of lead in white lead.

11. Perfectly pure tin, lead, zinc, and aluminum all look alike. What properties or conduct would enable you to tell any one of these from the others?

12. Name the properties and conduct of lead that make possible its use (*a*) as a lining of the chambers used in the manufacture of sulfuric acid (§ 346, 2); (*b*) for water pipes; (*c*) for making litharge; (*d*) as negative plates in storage batteries.

FOR HONOR STUDENTS

1. Read one of the chapters listed, and either write a theme on the subject or report orally to the class: Chapter VII (entitled "The Chemistry behind Electric Batteries") in Volume II of "Chemistry in Industry"; Chapter XIV (entitled "Paints, Varnishes, and Colors") in Volume II of "Chemistry in Industry."

2. Collect a set of samples of various materials that contain lead or tin, label them, and exhibit to the class.

CHAPTER XLIV

GOLD AND PLATINUM

710. ***Introduction.*** Gold and platinum suggest valuable coins and jewelry to most people, because the other uses of these metals are not very familiar. The two metals have some things in common, in that they are very heavy metals, not acted on by air or water, much more important as free metals than as compounds, high-priced, and much used in jewelry.

In many respects they differ greatly. Gold has been known and prized from the very earliest times, while any considerable knowledge of platinum dates from the discovery of the Russian deposits about the middle of the last century. Gold is yellow, platinum silvery like tin; gold is very soft, platinum rather hard; gold has comparatively few uses, platinum many; we measure the value of everything by the amount of gold it is equal to, but platinum is (with wide variation) about five times as valuable as gold.

Gold

711. Properties. Gold is a very heavy bright-yellow metal, a good conductor of electricity. It is the most malleable and ductile of the metals. It can be rolled or beaten into sheets so thin that a pile of 100,000 would be only 1 millimeter thick; or drawn into wire so fine that 2 miles of the wire weigh but 1 troy ounce. Its melting point (1063°) is much below that of platinum. It is quite soft and is usually alloyed with copper or silver to give it the hardness required for most practical uses. The degree of fineness is expressed in terms of *carats*, pure gold being 24 carats; the gold used for jewelry is usually 18 carats, 18 parts being gold and 6 parts either copper (yellow gold) or nickel and silver (white gold). Gold coinage is 90 per cent gold and 10 per cent copper. Gold is the standard of value; that is, by "dollar" we mean $\frac{3}{62}$ of a troy ounce of gold, which those who wish to use it in trade may get in five-dollar or ten-dollar pieces with its genuineness and weight certified by the government's stamp.

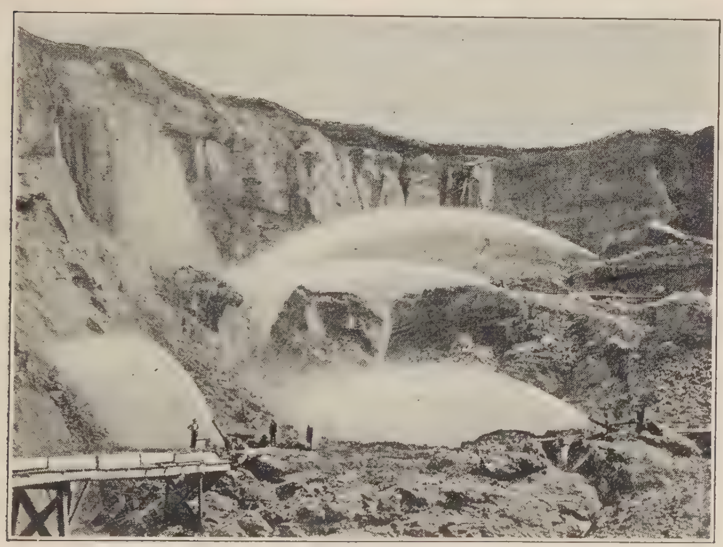


FIG. 316. Breaking down gold-bearing deposits by streams of water

712. Occurrence. South Africa produces the most gold. The United States produces about one seventh of the world's supply, Alaska, California, Colorado, and South Dakota leading in its production. Traces of it are found in almost all soils and even in sea water, but the cost of its production from such sources far exceeds the value of the metal extracted.

713. Extraction. The extraction of gold is accomplished in a number of ways, according to the character of the deposit. In *placer* mining the gold-bearing sand is washed by a current of water which is so regulated that particles of light weight are swept away, while the heavier gold is obtained as a sediment. In *hydraulic* mining the earth and sand are swept into sluices by powerful streams of water operated by pumps (Fig. 316). In *quartz* mining the quartz is stamped to powder and is then washed over copper plates, the surfaces of which have been coated with mercury (amalgamated). The particles of gold stick to the mercury or dissolve in it, the gold being recovered by distilling off the mercury. In other cases the ore is treated with solutions of chemicals that dissolve the gold, the gold being later recovered by electrolysis. A good deal of gold is obtained as a by-product in refining copper, silver, and lead.

714. Chemical conduct. Gold is not attacked by any one of the common acids; aqua regia easily dissolves it, forming *chlorauric acid* ($HAuCl_4$). Fused alkalies also attack it. Most oxidizing agents are without action upon it, and in general it is not an active element.

Platinum

715. Properties. Platinum is a grayish-white metal of high luster and is very malleable and ductile. It has a relatively high melting point (1755°), high density (21.45), and is a good conductor of electricity. In finely divided form it has the ability to adsorb gases, especially oxygen and hydrogen. These adsorbed gases are in a very active condition resembling the nascent state, and can combine with each other at ordinary temperatures. A jet of hydrogen or coal gas directed upon spongy platinum quickly ignites.

716. Occurrence and production. Like gold, platinum is found in metallic grains in the sand and gravel of streams

(Fig. 317), and is placer mined. In recently discovered South African deposits the grains are embedded in rock. A considerable quantity of the metal is annually recovered in the electrolytic refining of other metals, especially of nickel, gold, and copper. It is always alloyed with other similar but still rarer metals. Of the world's production up to the present time, Russia has produced about 90 per cent, and Colombia about 7 per cent. The greatest deposits are in Russia.

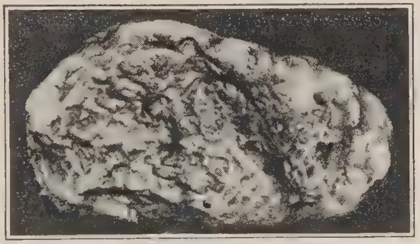


FIG. 317. The Demidoff nugget

This nugget, now in the Demidoff Museum in Leningrad, is the largest mass of platinum ever found. It weighs 7837 g. (21 lb. troy). (By courtesy of G. F. Kunz)

717. Chemical conduct. Platinum is a very inactive element chemically and is not attacked by any of the common acids. Aqua regia dissolves it slowly; it is also attacked by fused alkalies, and by chlorine but not by oxidizing agents. It forms alloys with many metals.

718. Platinum as a catalyst. Platinum is remarkable for its property of acting as a catalyst in a large number of chemical reactions, and mention has been made of this use of the metal in connection with the manufacture of sulfuric acid (§ 346) and nitric acid (§ 294). For this purpose some porous or fibrous substance, such as asbestos, is soaked in a solution of chloroplatinic acid and then ignited. The platinum compound is decomposed and the platinum deposited in very finely divided form. Asbestos prepared in this way is called *platinized asbestos.* The catalytic action seems to be in part connected with the property of adsorbing gases and rendering them nascent. Some other metals possess this same power, notably *palladium,* which is remarkable for its ability to adsorb hydrogen.

719. Applications. Platinum is very valuable as a material for the manufacture of chemical utensils which are required to stand a high temperature or the action of strong reagents. Platinum crucibles, dishes, forceps, electrodes, and similar articles (Fig. 318) are indispensable in the chemical laboratory. A considerable percentage of the supply of the metal is used in dentistry. In the industries platinum is used as a catalytic material in a number of reactions, and in the manufacture of a great variety of electrical apparatus such as resistance thermometers and X-ray and radio tubes.

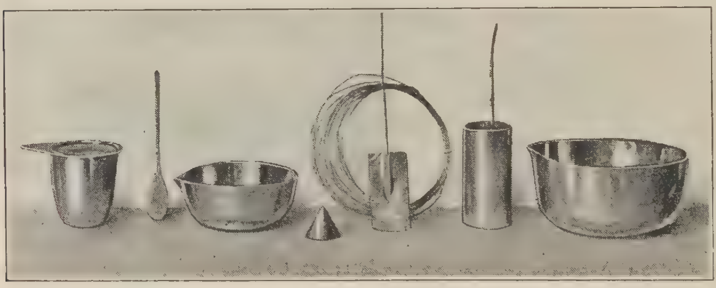


FIG. 318. Some laboratory utensils made of platinum

A large fraction of the annual production is used for jewelry. Its use in jewelry is due primarily to its high cost. It is unfortunate that it should be so used, because of the limited supply and its importance in necessary industries. Of the total production of platinum, jewelry absorbs about 60 per cent. The remainder is rather evenly divided between dentistry, chemical uses, and electrical uses.

720. Chloroplatinic acid (H_2PtCl_6). When platinum is dissolved in aqua regia and the solution is evaporated to dryness, orange-colored crystals of *chloroplatinic acid* (H_2PtCl_6) are obtained. The potassium and ammonium salts of this acid are nearly insoluble in water and in alcohol. These facts are important in chemical analysis.

CHAPTER SUMMARY IN QUESTION FORM

1. (*a*) Give three properties which gold and platinum have in common, and (*b*) state three respects in which these metals differ.

2. "The gold used for jewelry is 18 carats." (*a*) What is meant by the term "18-carat gold"? (*b*) Give two reasons why pure gold is not used for jewelry.

3. Give the composition of (*a*) a gold coin; (*b*) yellow gold; (*c*) white gold.

4. Mention three ways of extracting gold from gold deposits.

5. How does each of the following reagents act upon gold? (*a*) hydrochloric acid; (*b*) sulfuric acid; (*c*) nitric acid; (*d*) aqua regia.

6. State how platinum ranks with other metals in (*a*) density; (*b*) melting point; (*c*) malleability; (*d*) ductility; (*e*) conductivity; (*f*) ability to resist the action of acids.

7. Where are the largest known deposits of platinum located?

8. (*a*) What is a catalyst? (*b*) Why is platinum such a good one?

9. (*a*) Mention some of the uses of platinum. (*b*) Why is it used in jewelry?

10. What reagent dissolves both platinum and gold?

THOUGHT QUESTIONS

1. Platinum resembles tin, zinc, aluminum, and silver in appearance. How could you distinguish it from all these metals?

2. What action would take place if a piece of pure silver were dipped into a solution of (*a*) a gold compound? (*b*) a platinum compound? (*c*) In what process is advantage taken of this action?

3. Should a platinum crucible be used for melting lead?

4. Will nitric acid act on (*a*) pure gold? (*b*) gold coin?

FOR HONOR STUDENTS

1. Visit a jeweler and find out how he tests the purity of gold.

2. Read Chapter I ("Catalysis — a New Factor in Industry") in Volume II of "Chemistry in Industry," and write a theme on the subject or report the interesting facts to the class orally.

CHAPTER XLV

SOME LESS FAMILIAR ELEMENTS

721. *Introduction.* In this chapter we shall make the acquaintance of a number of metals, not often seen, but of great industrial importance. All of them form many compounds, yet in disguised dress the free metals are more important than their compounds. Few of them are ever prepared as *pure* metals; they are alloy materials or are used in the production of other metals. They act, as it were, an important part in the play — but behind the scenes.

Manganese

722. Occurrence and properties. It will be recalled that in the preparation of both oxygen and chlorine the oxide MnO_2 was used. This compound occurs in nature as the mineral *pyrolusite* and is the ore from which manganese and its compounds are prepared. The largest deposits are in Russia, India, and Brazil, but during the World War, when it was difficult to secure adequate supplies from these countries, considerable manganese ore was mined in the United States.

The metal is hard and brittle and closely resembles iron in appearance and in many of its properties. It liberates hydrogen from dilute acids and from water.

723. Metallurgy. The pure metal is of little importance. By reducing a mixture of oxides of iron and manganese there are obtained alloys of the two metals, known as *spiegeleisen* and *ferromanganese*, the latter having the higher percentage of manganese. These alloys are of the greatest importance in the steel industry. Manganese not only makes the steel very hard, but it removes the sulfur and oxygen that cause weak spots in steel rails. *Manganin* (Cu, 84 per cent; Mn, 12 per cent; Ni, 4 per cent) has important uses in electrical instruments as resistance wire. *Manganese bronze,* containing chiefly manganese and copper, resists corrosion.

724. Compounds of manganese. Hitherto we have thought of an element as either acid-forming or base-forming, the metals being base-forming. There are, however, a number of elements that are metals in all physical properties, and in *low valences* form hydroxides that are *bases*; but their oxides of *higher valences* are acid anhydrides. The chemistry of such a metal is not easy to understand because of the changes in valence that take place with corresponding oxidation and reduction reactions.

Manganese is a metal of this kind. It forms not only salts like other metals, but also unstable acids that are strong oxidizing agents of much practical importance.

725. Manganese salts. Manganese resembles iron in that it acts as both a bivalent and a trivalent metal. The *manganous salts,* in which the metal is bivalent, are the only important ones. These have formulas similar to the ferrous salts and resemble them in many of their chemical properties. Most of them are hydrated and pink in color. Examples are the sulfate, $MnSO_4 \cdot 4\ H_2O$, and the chloride, $MnCl_2 \cdot 4\ H_2O$.

726. Permanganic acid ($HMnO_4$); potassium permanganate ($KMnO_4$). Potassium permanganate is a salt of the unstable *permanganic acid* ($HMnO_4$). It is the easiest permanganate to prepare in pure condition, and forms deep-purple crystals readily soluble in water.

727. Oxidizing properties of potassium permanganate. Potassium permanganate is remarkable for its strong oxidizing properties, especially in the presence of an acid. When sulfuric acid is present the reaction takes place in such a way that *both the potassium and the manganese are changed into sulfates,* with the liberation of oxygen, as shown in the equation

$$2\,KMnO_4 + 3\,H_2SO_4 \longrightarrow K_2SO_4 + 2\,MnSO_4 + 3\,H_2O + 5\,O$$

Under ordinary conditions, however, the reaction does not take place unless a third substance is present which can be oxidized. The oxygen is not given off in the free state, but is used up in effecting oxidation.

Thus, ferrous sulfate is oxidized to ferric sulfate:

$$10\,FeSO_4 + 5\,H_2SO_4 + 5\,O \longrightarrow 5\,Fe_2(SO_4)_3 + 5\,H_2O$$

It is used as a powerful oxidizing agent in the laboratory, and as a disinfectant.

Chromium

728. General. Chromium is a hard metal about as heavy as iron. The only important ore is *chromite* or *chrome iron ore,* which has the composition $FeCr_2O_4$. This ore is found in many places, but the commercial supply comes chiefly from East Africa. The pure metal is rarely prepared, but the alloy *ferrochromium* is made by reducing a mixture of iron oxide and chromium oxide with carbon in an electric furnace. This rich alloy is melted with steel to produce chromium steel. *Nichrome* is an alloy of nickel and chromium, much used for electrical resistance in heaters (*A*, Fig. 319). Other alloys have already been mentioned (§§ 640, 654).

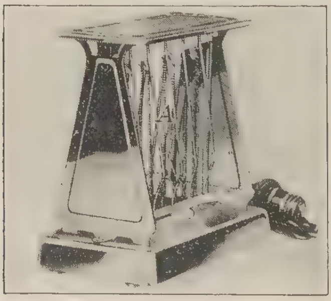


FIG. 319. Electric toaster

Resistance wire of nichrome is used in electric toasters and similar heating appliances

729. Compounds of chromium. Like manganese, chromium acts both as a base-forming and as an acid-forming element. All its compounds are colored; hence the name *chromium*, which is derived from a word meaning "color."

730. Chromic hydroxide ($Cr(OH)_3$); chromic salts. Chromic hydroxide is a greenish compound. It is insoluble and can therefore be prepared by precipitation. It dissolves in acids, forming the corresponding *chromic salts.* These are green or violet in color and have formulas similar to the ferric salts, such as $CrCl_3 \cdot 6\,H_2O$. They are used as mordants (§ 617) and in tanning leather.

731. Chromates. The chromates are salts of the unstable *chromic acid* (H_2CrO_4), and as a rule are yellow in color. Most of the chromates are insoluble and can be prepared from the soluble potassium salt by precipitation. In the case of lead chromate the equation is as follows:

$$Pb(NO_3)_2 + K_2CrO_4 \longrightarrow \underline{PbCrO_4} + 2\,KNO_3$$

Lead chromate (*chrome yellow*) and barium chromate are used as yellow pigments.

732. Potassium dichromate ($K_2Cr_2O_7$). When potassium chromate is treated with sulfuric acid, the potassium salt of *dichromic acid* ($H_2Cr_2O_7$) is formed:

$$2\,K_2CrO_4 + H_2SO_4 \longrightarrow K_2Cr_2O_7 + K_2SO_4 + H_2O$$

This is the best-known dichromate and the most familiar chromium compound. It forms large brilliant crystals of a red color and is rather sparingly soluble in water. Potassium dichromate, as well as the corresponding sodium salt ($Na_2Cr_2O_7$), finds use in many industries as an oxidizing agent, especially in the preparation of organic substances and in the construction of several kinds of electrical batteries.

733. Oxidizing action of potassium dichromate. When a dilute solution of potassium dichromate or sodium dichromate is treated with sulfuric acid, no reaction apparently takes place. If, however, a third substance is present that is capable of oxidation, the dichromate gives up a portion of its oxygen to this substance, and both the potassium and the chromium are converted into sulfates. The oxidation of ferrous sulfate by potassium dichromate is a good illustration, the reaction being represented in two steps:

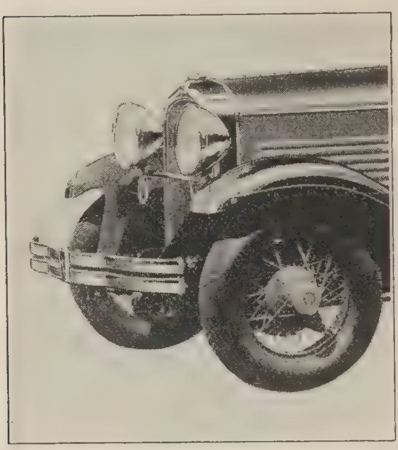


FIG. 320. Chromium plating

The headlights, radiators, and bumpers of automobiles are often chromium plated

$$K_2Cr_2O_7 + 4\,H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4\,H_2O + 3\,O$$
$$6\,FeSO_4 + 3\,H_2SO_4 + 3\,O \longrightarrow 3\,Fe_2(SO_4)_3 + 3\,H_2O$$

734. Chromium electroplating. In recent years chromium has come into use for electroplating automobile parts and similar objects (Fig. 320). It can be plated on brass, nickel, copper, or iron, and forms a surface that is harder than steel, is not corroded by weather or by dilute reagents, and retains its luster remarkably well. The electrolyte usually consists of a solution of chromic acid together with some sulfate ions.

A Variety of Elements

735. General. About half of the ninety known elements have been described in the foregoing pages, some of them very briefly. An acquaintance with the other half is not at all necessary, but a few words about some of them are desirable.

Some of them are not at all rare. Thus, *titanium,* an element resembling silicon though more metallic, is much more abundant than either carbon or sulfur.

Others are so rare that the cost of production is prohibitive even though they have very useful properties. Still others could not be produced in appreciable quantities from any known source at *any* cost.

736. Titanium in the silicon family is an abundant element, occurring chiefly as the oxide TiO_2, called *rutile,* and as a constituent of certain iron ores (*ilmenite*). Its oxide, reduced together with iron oxide, gives the alloy *ferrotitanium,* used in making titanium steel. This is very strong and tough, and is especially suited to steel rails designed to stand heavy wear (railway curves and terminals). A paint body, *titanox* (§ 707, 2), is in some important respects better than white lead in paints, and various compounds of titanium now have a number of minor uses.

737. Zirconium is found in abundance in Brazil in the form of the oxide ZrO_2. This oxide has an exceedingly high melting point. Bricks made of it are used (under the name *zircite*) for lining furnaces.

738. Vanadium occurs in considerable quantities in the American mineral *carnotite* (§ 749) and in certain sulfides found in Peru. *Ferrovanadium,* like ferrotitanium, is used in producing special grades of steel (Fig. 321), particularly when great toughness is desired (automobile parts). Its compounds are used as photographic developers, as catalytic reagents in the dye industry (aniline black) and in making sulfuric acid (§ 346), as coloring materials in glass, and as mordants.

739. Tungsten ores are produced in fairly large quantities. It has been found possible to draw the metal into very fine wire, which has replaced carbon as a filament for electric lamps. Its melting point is very high (3370°), so it can be safely heated to a *white* heat. The consumption of electrical energy for a given candle power is so low that the lamp is about three times as efficient as the older (carbon) lamp. The metal is a good conductor, and so the wire must be very fine and rather long to give the necessary electrical resistance. The metal has replaced platinum for electrical contacts in switches, in telephone jacks, and in automobile vibrators. Ferrotungsten is used in making steel designed for lathe tools, since such steel is very hard and can be heated to a red glow without losing temper.

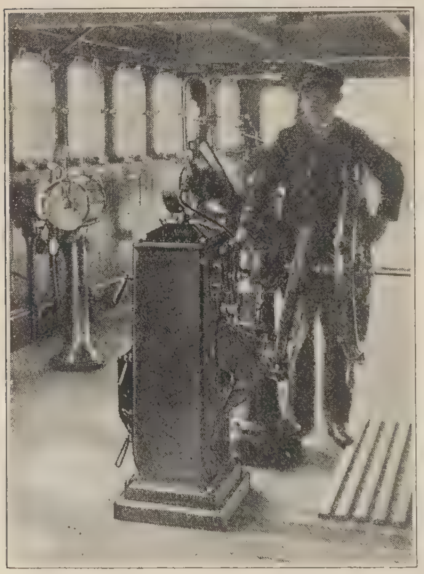


FIG. 321. The Sperry gyrocompass

The gyrocompass depends upon the rotation of a wheel of vanadium steel. The wheel rotates at 8600 revolutions per minute, and must resist wear and strain. The picture shows the bridge of the ship *Leviathan* with the compass in the foreground

740. Molybdenum is a metal similar to tungsten but of lower melting point and is more easily oxidized. Ferromolybdenum is used in making molybdenum steel, which resembles tungsten steel in many ways. Compounds of molybdenum are used in chemical analysis, and for coloring glazes and dyeing silk, wool, and leather. The colors produced are chiefly blue.

741. Uranium oxide is used in making the greenish-yellow glass so familiar in lamp shades, and as a pigment in china glazes.

742. Selenium, an element in the sulfur family, is obtained as a by-product in refining copper. It is a nonconductor of electricity *in the dark*, but becomes a fairly good conductor *when exposed to light*. This has led to its use in automatic fire alarms and for regulating automatic gas buoys at sea. Added to glass it produces a fine red color (§ 429), such glass being used for automobile tail-lights and railway lanterns. It is also used to produce red enamels.

743. Iridium gives a very hard alloy with platinum and is used for pen points, compass bearings, and standard weights and measures.

744. Palladium is only about half as heavy as platinum, has a much lower melting point, and is harder. It is used as a solder for platinum, for making graduated scales in scientific instruments, and as a substitute for platinum in jewelry. In the form of a powder it is a remarkably active catalytic agent.

CHAPTER SUMMARY IN QUESTION FORM

1. Name two elements in the laboratory preparation of which manganese dioxide is used.

2. (*a*) Make a list of the metals mentioned in this chapter, and (*b*) state one important use of each.

3. (*a*) Name an acid-forming element, and (*b*) give the formula for one acid which it forms; (*c*) also name a base-forming element, and (*d*) give the formula for a base which it forms.

4. Name two elements which act both as acid-forming elements and as base-forming elements.

5. One of the most useful of the compounds of manganese is potassium permanganate. (*a*) Describe its appearance. (*b*) What property makes it a useful compound? (*c*) Is the manganese in this compound an acid-forming or a base-forming element?

6. State (*a*) the names and (*b*) the chief uses of two important alloys of chromium.

7. Mention two important uses of chromium.

8. Give (*a*) the name, (*b*) the formula, (*c*) the appearance, and (*d*) the use of the potassium salt of dichromic acid.

9. State one item of interest about each of the "variety of elements" mentioned in this chapter.

THOUGHT QUESTIONS

1. For what purpose is manganese dioxide used in the glass industry?

2. Manganese dioxide in powdered form closely resembles powdered charcoal. How could you easily distinguish between the two?

3. When manganese dioxide is used in the preparation of chlorine, what compound of manganese is formed?

4. What important sulfates have we studied that are (*a*) colorless? (*b*) colored?

5. When sulfurous acid (colorless) is added to a solution of potassium permanganate (colored), a colorless solution results. Explain.

6. The common cleaning fluid used in the laboratory for cleaning test tubes and beakers consists of a mixture of sodium dichromate and sulfuric acid. Where does its efficiency lie?

FOR HONOR STUDENTS

1. Form an exhibit of as many samples as possible of the metals mentioned in this chapter, their alloys, and their compounds.

2. Read one of the chapters listed, and report the facts that interest you most: Chapter XIV (entitled "Metals, Old and New") in "Creative Chemistry"; Chapter XVI (entitled "Chemistry, Radio, and Incandescent Lamps") in Volume II of "Chemistry in Industry."

CHAPTER XLVI

THE STORY OF RADIUM

745. ***Introduction.*** In the spring of 1921 Madame Curie (Fig. 325), professor of physics at the University of Paris, paid a visit to the United States that attracted much attention in the daily press. Many honors were bestowed upon her by universities and scientific societies. By popular subscription the women of our country raised the sum of $120,000, with which was purchased *one gram* of radium in the form of radium bromide, — the costliest of all materials, — and on their behalf this was presented to Madame Curie by the President of the United States in the White House at Washington. Never before has the visit of a professor from a European country attracted so much attention. Why was this?

746. Discovery of radium. To answer the question asked above we must go back some thirty-five years. In 1895 the German physicist Röntgen discovered a wonderful form of *radiation* capable of passing through glass and acting upon a photographic plate much as light acts, but not visible to the eye. These were the *X rays,* by means of which the surgeon takes pictures of bones in the body.

It occurred to the French physicist Becquerel that similar radiations might be given off by those substances that shine faintly in the dark and are called *phosphorescent.* Among others he tried some compounds of the rare metal *uranium,* wrapping them in black paper to keep out light and placing them on a photographic plate. Immediately under these salts the plate was affected as if by light, so there *was* a radiation of some kind. Two facts of great importance were soon discovered: (1) these new rays could not pass through metal objects, so that radiographs could be made with them just as with X rays (Fig. 322); (2) when brought *near* these uranium compounds a charged electroscope was rapidly discharged (Figs. 323, 324), showing that the air all around them was an electrical conductor, which is not true of ordinary air. This new property of uranium compounds of giving off rays was called *radioactivity*.

FIG. 322. A radiograph of some metal objects

747. Work of the Curies. At the suggestion of Becquerel his associate Pierre Curie, together with his Polish bride Madame Curie, began a study of radioactivity. They found that *pitchblende*, U_3O_8 (the common ore of uranium), was *four times* as active as pure uranium oxide, and they argued that the real radioactive substance is an impurity in pitchblende that is not entirely removed in the process of getting uranium compounds. By long-continued work on tons of ore they finally isolated a minute quantity of the chloride of a new element four million times as radioactive as uranium, which they named *radium*.

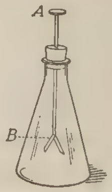


FIG. 323. A charged electroscope

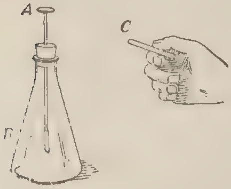


FIG. 324. A discharged electroscope

In 1906 Monsieur Curie was killed in a street accident, and Madame Curie continued the work, in which many others now engaged. She found the atomic weight of radium to be 226, and this weight, as

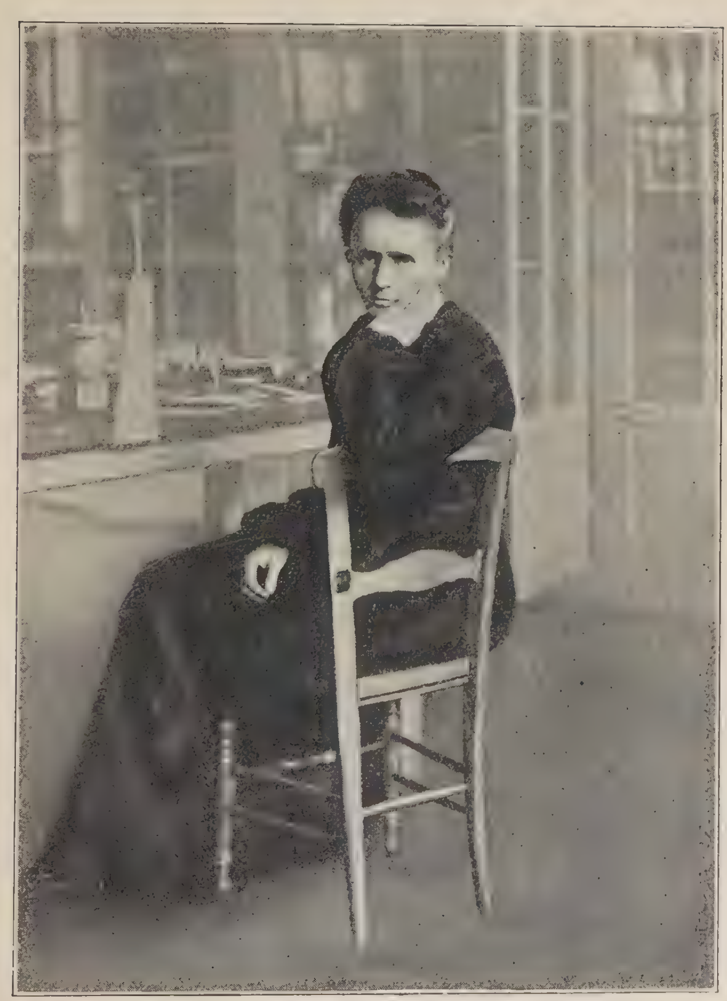


FIG. 325. Madame Curie in her laboratory in Paris

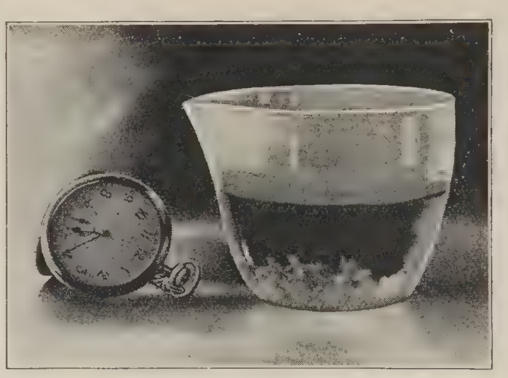
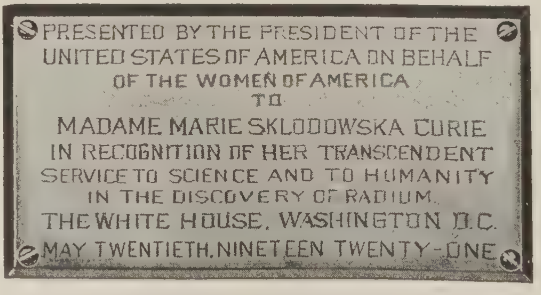


Fig. 326. Picture taken in the laboratory of the Standard Chemical Company, showing the crystallization of the radium bromide which the women of America presented to Madame Curie on the occasion of her visit to America in 1921. A second gram of radium was presented to Madame Curie during a visit in 1929, which she dedicated to the use of her native country, Poland



PRESENTED BY THE PRESIDENT OF THE
UNITED STATES OF AMERICA ON BEHALF
OF THE WOMEN OF AMERICA
TO
MADAME MARIE SKLODOWSKA CURIE
IN RECOGNITION OF HER TRANSCENDENT
SERVICE TO SCIENCE AND TO HUMANITY
IN THE DISCOVERY OF RADIUM.
THE WHITE HOUSE, WASHINGTON D.C.
MAY TWENTIETH, NINETEEN TWENTY-ONE

Fig. 327. Inscription on the box containing the radium bromide presented to Madame Curie by the women of America

well as all the chemical properties of the compounds of radium, placed the element in the space at that time vacant below barium in the calcium family. A minute quantity of the metal itself was isolated by Madame Curie in 1910.

748. Quantity of radium available. In all other instances when a new and very interesting element has been found, energetic search has soon provided a supply. This was not so with radium. It was soon found out that radium occurs in all uranium ores *and in no others*. A still more surprising fact is that in all these ores *the ratio between the uranium and the radium is constant*, being about 1 part of radium to 3,400,000 parts of uranium. There is no hope of finding any other ores of radium, and uranium ores themselves are very rare.

749. Production of radium. The uranium ores available at the time of the discovery of radium were the low-grade pitchblende deposits of Austria, long worked for coloring glass. Later a rare mineral, *carnotite*, was found in the deserts of Colorado and Utah which averaged about 2 per cent U_3O_8, and from this source the United States produced more radium than the rest of the world. In 1922 remarkable deposits of pitchblende were discovered in the Belgian Congo. This ore is shipped to Belgium, and that country now produces all the radium. About 15 tons of the ore will produce 1 g. of radium. Deposits of a similar ore have recently been found in Canada.

Radium compounds are sold wholly upon the basis of their radium content, and are spoken of as though they were the element itself. Thus, the United States produced in all, from 2 per cent ores, about 170–180 g. of *radium* (as chloride or bromide), which sold for about $110,000 per gram *radium*. At present the Belgian company, using a richer ore, is selling it at about $70,000 per gram, but this includes a large profit.

750. Disintegration of radium. As one looks casually at a sample of a radium salt, such as the chloride, there is little to distinguish it from any other white salt, such as its first cousin barium chloride. But if we could watch many millions of radium *atoms* we should see a wonderful sight. Every now and then we should see one of these atoms explode violently, much as now and then a grain of pop corn explodes as we warm the corn, and it then ceases to be a radium atom.

These explosions take place at such a rate that one half of any given sample of a radium compound will cease to be radium in 1580 years. This is known as the *half-life period* of radium. As a result of these explosions all compounds of radium (containing uncounted billions of atoms) are constantly giving off three kinds of so-called *rays*. These are called alpha (α) rays, beta (β) rays, and gamma (γ) rays, these being the first three letters in the Greek alphabet.

751. Nature of radioactive rays. The alpha rays are doubly charged helium atoms (He^{++}), each helium atom having left two electrons behind as it was driven out of the nucleus of the radium atom. They are shot off with a velocity of about 20,000 mi. per second, but have little penetrating power. They are stopped by a sheet of paper or the thinnest metal foil.

The beta rays are electrons, shot off with a velocity of approximately 100,000 mi. per second. They have greater penetrating power than the alpha rays, but are stopped by relatively thin sheets of metal.

The gamma rays are not moving particles like the alpha and beta rays, but are vibrations in the ether like light. They correspond to the flash of light that often accompanies an ordinary explosion. They move with the same velocity as light (186,000 mi. per second), but differ from light in having very short wave-lengths — much shorter than those of X rays.

The rate of these explosions is kept up very steadily all the time, and is not changed by any means as yet tried (such as very high or very low temperatures); and all compounds of radium act just alike in the rate of these explosions.

752. Where radium comes from. Radium is decomposing at a rate that puts its half-life period at 1580 years, and yet the rocks in which it is found are hundreds of thousands of years old. Why has any radium survived? Plainly it must be in constant process of formation from some other element, and it has been proved that this parent element is *uranium.* Uranium is therefore also going to pieces (it is radioactive), *but at a much slower rate than radium.* So all uranium ores must contain radium, and none can contain very much. The quantity of radium present is merely the result of equilibrium between the rate of its formation and the rate of its disintegration. So we see why we shall never find rich radium ores.

753. Where radium goes to. From the facts so far described it might be supposed that the explosion of a radium atom blows it up completely into the separate protons and electrons of which it is composed, just as the explosion of a mine under a brick wall would blow the wall into bricks (protons) and mortar dust (electrons). The real picture of what happens is not this way at all, but is as follows:

There is a long series of these radioactive elements, at least fifteen, related to each other in a remarkable way. When any one of them explodes, it drives out of its nucleus *either a helium nucleus* (He^{++}) *or an electron* (rarely, one of each), and so is changed into the next lower kind of atom in the series. The life of some of these elements is very long; in other cases it is very short — merely a few hours or even in one case a fraction of a second.

The atomic weight of uranium is 238 and that of radium 226 — a difference of 12 units. So between uranium and radium three successive explosions have occurred in which an alpha ray (He^{++}, atomic weight, 4) has been shot off. Two others have resulted in driving out beta rays (electrons), making four elements in all *between* uranium and radium.

When the last one of the long series of radioactive elements explodes, the atom formed is *an isotope of lead* (atomic weight, 206), and such lead is always found in uranium ores. One of the most violent of all these explosions is that of the gaseous element *radon*, which is formed directly from radium. It melts at $-71°$ and boils at $-62°$. Its half-life period is 3.85 days. Radium *directly* changes into radon; by a succession of explosions it *finally* becomes an isotope of ordinary lead.

754. Internal energy of radium. If the explosions of the radium atoms and of those of other radioactive elements are as terrific as we have pictured them, and if the alpha and beta rays are shot off with such incredible velocities, the energy set free must be much greater than that of any known reaction between elements. A radium compound actually does keep warm all the time. It is estimated that 1 g. of radium *hourly* evolves about 120 cal. of heat, and this is kept up for the entire life of the element. From this it can be computed that the total energy given off by a gram of radium in disintegrating into lead is about 250,000 times the heat of combustion of a gram of carbon.

755. Why radium is so important. The way in which the atoms of radium explode, the products formed in the explosion, and the similar conduct of all the elements of the series in which radium has a place, make it certain that here is a series of elements, of which radium is the best known, *whose atoms have an elaborate structure* made up of helium atoms and electrons. These must be arranged in such a way as to hold an enormous store of energy — much as a compressed spring holds energy. The very fact that radium resembles the other elements in all ways, apart from radioactivity, having its natural place in the periodic table, make it probable that all the other elements have a similar structure but explode so rarely that we never know it, and they probably have very much less internal energy. Indeed, two well-known elements — potassium and rubidium — have been reported as being slightly radioactive.

All these facts taken together, and strengthened by many physical and electrical experiments, resulted in the theory of the structure of all atoms described in Chapter XIV. So radium has played a great part in developing our modern view of the structure of the atom and the nature of electricity.

The fact that alpha rays are helium nuclei (of four protons each), and *not* individual protons, makes it seem probable that the protons in the nuclei of all atoms are, to some extent at least, arranged in groups of four; but as yet we know little about the arrangement of protons and electrons within the nucleus.

756. Practical uses of radium. Such a remarkable material as radium could hardly fail to find useful applications. The rays emitted from radium, radon, and other members of the series, particularly the gamma rays, produce many chemical and physiological effects. They disintegrate glass, water, and many other substances. They render certain materials luminous in the dark, and enamel paints containing radium are used to illumine the hands of watches, the push buttons of electric lights, and the keyholes of doors. They produce severe burns upon the skin like those of X rays. They kill bacteria and other microörganisms.

This latter property has led to the hope that exposure to the radiations of radium compounds may, under proper conditions, prove to be of service in effecting a cure for some diseases of the skin and for cancer. It is not possible to say as yet to what extent these hopes will be realized. Certain forms of cancer have almost certainly been cured in this way, and the progress of other forms has been delayed.

757. Radioactive thorium. Madame Curie discovered that the rare element *thorium* exhibits properties very similar to those of uranium. It gives rise to a similar series of radioactive elements by successive decomposition, producing the same varieties of radiation as the other series. Uranium and thorium are the elements of greatest atomic weight, and this suggests the idea that possibly elements of still higher atomic weight may have existed at some time, but that they have disintegrated into ones of smaller atomic weight which are not radioactive.

CHAPTER SUMMARY IN QUESTION FORM

1. Name two persons whose scientific investigations paved the way for the discovery of radium by the Curies.

2. What was the nature of the discovery of each of these men?

3. Give two ways of telling whether or not an element is radioactive.

4. The Curies found that the uranium oxide ore was more radioactive than the pure uranium oxide. (*a*) What assumption did they make to explain this fact, and (*b*) to what discovery did this assumption lead?

5. Name the two ores from which radium may be extracted.

6. (*a*) Name the so-called *rays* of radium, and (*b*) state a characteristic of each.

7. (*a*) What means does the chemist employ for starting and stopping ordinary chemical reactions? (*b*) Do these means enable the chemist to control the disintegration of radium?

8. Suppose you have 1 g. of radium. In about how many years will half of this be disintegrated?

9. Does there seem to be any possibility that a supply of fairly pure radium will ever be found?

10. Mention the chief uses of radium.

11. Mention some of the facts of radium disintegration that help to prove the modern theory of the structure of atoms.

THOUGHT QUESTIONS

1. In addition to radium, Madame Curie discovered another radioactive element, which she named polonium. Can you suggest a reason for selecting this name?

2. A clap of thunder travels at the rate of about 1100 ft. per second. Compare the speed of the sound with the speed of an alpha particle.

3. Does there seem to be any probability that the radium will ever be all disintegrated?

FOR HONOR STUDENTS

1. Read Chapter XV (entitled "The Wonders of Radium") in Foster's "The Romance of Chemistry," and report the important facts.

2. Write an account of the life of Madame Curie. (Consult any encyclopedia.)

APPENDIXES

A. CHEMICAL LIBRARY

Every high school should have at least a few books dealing in a popular way with topics of interest to students beginning chemistry. A large number of such books are available; all are interesting, and some as fascinating as any story of romance ever written. The titles of a few such books are given below. Prices can be obtained from any bookstore. A great deal of important literature bearing upon chemical topics may be had free of charge. This is true of the bulletins published by certain departments of the Federal government, especially the Department of Agriculture and the Department of Commerce Bureau of Mines, and the Bureau of Standards, Washington, D.C. A list of available bulletins may be obtained by addressing these departments.

Much that is interesting in regard to the subject will be found in the files of various periodicals. Every laboratory should subscribe for the *Journal of Chemical Education*, a monthly journal devoted to the interest of chemistry teachers (business manager, W. W. Buffum, care of The Chemical Foundation, Inc., New York City). Teachers of chemistry in secondary schools will find especially valuable the *Chemistry Leaflet*, published weekly as a supplement to the *Journal of Chemical Education*. In *School Science and Mathematics*, published nine times a year by The Central Association of Science and Mathematics Teachers (business manager, W. F. Roecker, 1439 Fourteenth Street, Milwaukee, Wisconsin), there are many articles of interest to chemistry teachers. The *Scientific American* also contains many interesting articles on chemical topics.

The most important of the books listed below are marked with an asterisk. The five books marked with a double asterisk are referred to a number of times in the text; at least these five should be available in every laboratory.

LIST OF SUPPLEMENTARY BOOKS

BAILEY. A Textbook of Sanitary and Applied Chemistry. The Macmillan Company.
BANCROFT. Applied Colloid Chemistry. McGraw-Hill Book Company.
BENSON. Industrial Chemistry. The Macmillan Company.
BIRD. Modern Science Reader. The Macmillan Company.
CALDWELL and SLOSSON. Science Remaking the World. Doubleday, Page and Company.
**CHAMBERLAIN. Chemistry in Agriculture. The Chemical Foundation, Inc., New York.
COLLINS. The Wonders of Chemistry. Thomas Y. Crowell Company.
CURIE, MARIE. Pierre Curie. The Macmillan Company.
CUSHMAN. Chemistry and Civilization. Richard G. Badger.
*DUNCAN. The Chemistry of Commerce. Harper and Brothers.
*DUNCAN. The New Knowledge. Harper and Brothers.
*DUNCAN. Some Chemical Problems of Today. Harper and Brothers.
*FARADAY. Chemical History of a Candle. Harper and Brothers.
*FINDLAY. Chemistry in the Service of Man. Longmans, Green, and Company.
FLINN. Popular Research Narratives. The Williams and Wilkins Company.
**FOSTER. The Romance of Chemistry. The Century Company.
*GEER. The Reign of Rubber. The Century Company.
*GRANT. Chemistry of Bread-Making. Longmans, Green, and Company.
*GREEN. Coal and Coal Mines. Houghton Mifflin Company.
HALE. American Chemistry. D. Van Nostrand Company.
HARROW. Eminent Chemists of our Time. D. Van Nostrand Company.
HARROW. The Romance of the Atom. Boni and Liveright.
*HART. Leavening Agents. Chemical Publishing Company.
*HAWK. What we Eat. Harper and Brothers.
*HENDRICKS. Everyman's Chemistry. Harper and Brothers.
**HOWE. Chemistry in Industry, Vol. I. The Chemical Foundation, Inc., New York.
**HOWE. Chemistry in Industry, Vol. II. The Chemical Foundation, Inc., New York.
*HOWE. Chemistry in the World's Work. D. Van Nostrand Company.
*HOWE and TURNER. Chemistry of the Home. Charles Scribner's Sons.
JENKS. Chemistry for Young People. Frederick A. Stokes Company.
*KENDALL. At Home among the Atoms. The Century Company.
MCPHERSON and HENDERSON. A Course in General Chemistry. Ginn and Company.
*MARTIN. The Story of a Piece of Coal. George Newnes, Ltd., London.
*MARTIN. Triumphs and Wonders of Modern Chemistry. D. Van Nostrand Company.
*MEADE. Story of Gold. D. Appleton and Company.
*MOORE. A History of Chemistry. McGraw-Hill Book Company.

MUIR. The Story of Alchemy. D. Appleton and Company.
PHILIP. Romance of Modern Chemistry. J. B. Lippincott Company.
*PRIESTLEY. The Discovery of Oxygen. The University of Chicago Press.
RAMSAY. Gases of the Atmosphere. The Macmillan Company.
**SLOSSON. Creative Chemistry. The Century Company.
SMITH. Chemistry in America. D. Appleton and Company.
SMITH. Story of Iron. D. Appleton and Company.
*SNYDER. Chemistry of Plant and Animal Life (popular). The Macmillan Company.
STEWART. Chemistry and its Borderland. Longmans, Green, and Company.
*STIEGLITZ. Chemistry in Medicine. The Chemical Foundation, Inc.
*SURFACE. Story of Sugar. D. Appleton and Company.
*TOTTINGHAM and INCE. Chemistry of the Farm and Home. Webb Publishing Company.
*TOWER. Story of Oil. D. Appleton and Company.
*VENABLE. A Short History of Chemistry. D. C. Heath and Company.
WARDALL and WHITE. A Study of Foods. Ginn and Company.
WOOLMAN and MCGOWAN. Textiles. The Macmillan Company.
*WOOD. Story of a Loaf of Bread. G. P. Putnam's Sons.
Scientific American Cyclopedia of Formulas. Munn and Company, New York City.
United States Department of Agriculture: (1) Composition of Foods, *Bulletin 28*, Office of Experiment Stations; (2) Nutritive Value of Foods, *Farmers' Bulletin 142*; (3) Some Forms of Food Adulteration and Simple Methods for their Detection, *Bulletin 100*, Bureau of Chemistry; (4) Industrial Alcohol, *Farmers' Bulletins 268, 269*; (5) Household Tests for the Detection of Oleomargarine and Renovated Butter, *Farmers' Bulletin 363*; (6) Canned Fruits, Preserves, and Jellies, *Farmers' Bulletin 203*; (7) Removal of Stains from Clothing and other Textiles, *Farmers' Bulletin 1474*. (Send to the Department of Agriculture, Washington, D.C., for list of available bulletins and select such as may be of interest.)
United States Bureau of Standards: Measurements in the Home, *Circular 55*; Common Materials used in the Home, *Circular 70*; Problem of Safety, *Circular 75*; Inks, *Circular 95*.

B. THERMOMETERS

A thermometer is the well-known instrument used for measuring temperatures. It consists of a glass bulb joined to a thick-walled glass tube which has a very small but uniform bore (Fig. 328). There are two kinds of thermometers in common use: the Fahrenheit (F.), ordinarily used in our homes, and the centigrade (C.), used for all scientific purposes. These differ only in the manner in which they are graduated. In their construction the bulb and a part of the tube are filled with mercury, and the bulb is then surrounded by melting ice. The mercury contracts as it reaches the temperature of the melting ice and remains stationary when this temperature is reached. The height of the mercury in the tube is then marked on the tube. The thermometer is next immersed in boiling water or steam (under a pressure of 1 atmosphere). The height to which the mercury rises is again marked on the tube. In the Fahrenheit thermometer the melting point of ice and the boiling point of water are marked 32° and 212° respectively, and the space between these two points on the tube is divided into 180 equal parts (degrees); in the centigrade thermometer the two points noted above are marked 0° and 100° respectively, and the intervening space on the thermometer tube is divided into 100 equal parts (Fig. 328). In other words, in the Fahrenheit system ice melts at 32° and water boils at 212°, while in the centigrade ice melts at 0° and water boils at 100°. The equal divisions on the tube may be extended below the melting point of ice and above the boiling point of water.

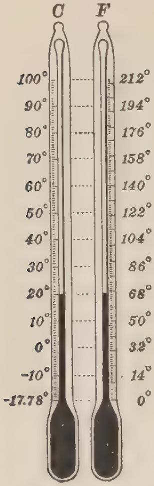


FIG. 328. The centigrade and Fahrenheit scales

It is easy to convert readings on the Fahrenheit scale into the corresponding readings on the centigrade scale and vice versa. It is only necessary to keep in mind that 180° on the Fahrenheit scale (the difference in degrees between the melting point of ice and the boiling point of water) equals 100° on the centigrade (or 1° F. equals $\frac{5}{9}$° C.) and that 32° F. is the same as 0° C. The above relations are expressed in the following equation:

$$\frac{C}{F-32}=\frac{5}{9}$$

Suppose we wish to convert 75° F. into centigrade reading: substituting 75 for F in the above equation, we have

$$\frac{C}{75-32}=\frac{5}{9}$$

Solving for C, we have

$$\begin{aligned} 9\,C &= 5(75 - 32) \\ 9\,C &= 215 \\ C &= 23.8° \end{aligned}$$

Similarly, if we wish to convert centigrade readings into Fahrenheit we substitute the centigrade reading for C in the equation given on page 560, and solve for F.

C. REDUCTION OF GAS VOLUMES TO STANDARD CONDITIONS

In a great many chemical operations, both in the laboratory and in manufacturing plants, it is necessary to measure the volumes of gases with accuracy under various conditions. The directions in Chapter V are not sufficient to enable one to make the necessary calculations, and a more complete explanation is here given for the guidance of those students who may become interested in this subject.

Variation of volume with pressure: Boyle's law. In Chapter V Boyle's law was stated as follows: *The volume occupied by a given weight of gas varies inversely with the pressure, provided the temperature of the gas remains constant.* Thus, if a given weight of a gas occupies a volume of 1000 cc. when subjected to a given pressure, it will occupy a volume of 500 cc. if the pressure is doubled, or of 2000 cc. if the pressure is diminished to one half. This means that for a given weight of a gas the product of the pressure into the volume will remain constant, no matter how either one may be altered. Designating the pressure and volume under one set of conditions by P and V, and under a different set by P_1 and V_1, Boyle's law may be stated thus:

$$PV = P_1V_1$$

Standard pressure. For practical purposes it is desirable to choose some *standard pressure* under which we will agree to measure all gas volumes. This is most conveniently chosen as the average pressure of the atmosphere at the sea level. This is equal to 1033 g. per square centimeter. In place of expressing the pressure in this way it is much more convenient to express it in terms of the height of the column of mercury which the pressure of the atmosphere will sustain. Expressed in this way the standard pressure is equal to the pressure exerted by a column of mercury 760 mm. in height, this being the average height of the barometer at the sea level.

Illustration of Boyle's law. The following example will not only make the meaning of the law clear but will also show how the law enables us to calculate the changes in the volume of a gas due to changes in pressure:

A gas measured under a pressure of 720 mm. had a volume of 620 cc. What volume will this gas occupy under standard pressure, 760 mm., the temperature remaining constant?

According to Boyle's law,

$$PV = P_1V_1$$

Substituting the values given in the problem, we have

$$760 \times V = 720 \times 620, \quad \text{or} \quad V = 587.4 \text{ cc.}$$

Variation of volume with temperature. If the pressure is held constant, all gases expand when the temperature is raised and contract when it is lowered, and it is a remarkable fact that the volumes of all gases change to the same extent for a given variation in the temperature. Let us suppose that the volume of a gas has been measured at 0° on the centigrade scale. Experiment has shown that for each degree the temperature is raised above 0°, the volume of the gas increases by $\frac{1}{273}$ of *the volume it occupied at 0°*. Similarly, for each degree the temperature is lowered below 0°, the volume diminishes by $\frac{1}{273}$ of the volume it occupied at 0°. To take a simple illustration: If the volume of a gas at 0° is 273 cc., then at 1° it will be 274 cc., while at − 1° it will be 272 cc. At 5° it will be 278 cc., while at − 5° it will be 268 cc. It is evident, then, that at this rate of change the volume at − 273° will be 0. Of course this cannot really happen, and experiment shows that before this temperature is reached all gases have changed into liquids or solids.

The absolute scale. For many purposes it has been found convenient to use a scale of temperature known as the *absolute scale,* on which the divisions are of the same size as those on the centigrade scale, but the zero point is at − 273° on the centigrade scale; that is, the temperature at which the volume of any gas would apparently become zero (see preceding paragraph). The

0° on the centigrade scale is then 273° on the absolute scale. On such a scale all temperatures are above the zero point. To convert readings on the centigrade scale to the corresponding ones on the absolute it is only necessary to add 273°. Thus, 20° C. = 20° + 273°, or 293° A., while −20° = −20° + 273°, or 253° A. Fig. 329 gives a comparison of the centigrade and absolute scales at a number of temperatures.

Charles's law. A general statement can now be made in regard to the effect of temperature on the volume of a gas: *The volumes occupied by a given weight of a gas at different temperatures are proportional to the absolute temperatures, provided the pressure remains constant.* If V and V_1 are the volumes at the temperatures T and T_1, then $V : V_1 = T : T_1$,

or
$$V = \frac{V_1 T}{T_1}$$

The above generalization is called Charles's law. This statement of the law is of more general application than that given in § 69, which does not involve a knowledge of the absolute scale. Both statements, however, are equally correct.

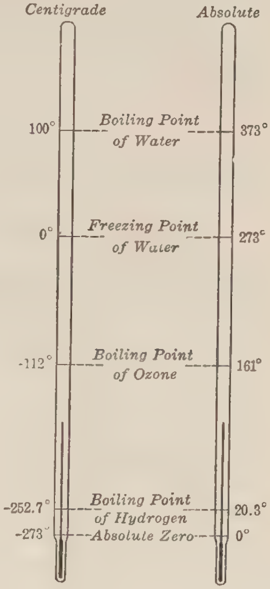


FIG. 329. Comparison of the centigrade with the absolute scale of temperature

Illustration of Charles's law. The following example will make the meaning of the law clear:

The volume of a certain gas measured at a temperature of 70° is 650 cc. What will be its volume at 10°, the pressure remaining unchanged? First reduce the centigrade readings to absolute:

$$70^\circ \text{ C.} = 70^\circ + 273^\circ = 343^\circ \text{ A.}; \; 10^\circ \text{ C.} = 10^\circ + 273^\circ = 283^\circ \text{ A.}$$

Then substitute the appropriate values in the above equation:

$$V = \frac{650 \times 283}{343}, \quad \text{or} \quad V = 536.3 \text{ cc.}$$

Variations in volume due to changes in both pressure and temperature. In case both pressure and temperature change, then the correction may be made for each in succession, as illustrated in the following example:

A certain weight of gas measured 500 cc. at a temperature of 100° when subjected to a pressure of 760 mm. Calculate the volume which this gas will occupy at a temperature of 50° and a pressure of 740 mm.

First make the correction for pressure:

$$PV = P_1V_1$$

$$740 \times V = 760 \times 500, \text{ or } V = 513.5 \text{ cc.}$$

Next make the correction for temperature:

$$V = \frac{V_1T}{T_1}, \text{ or } V = \frac{513.5 \times 323}{373}, \text{ or } V = 444.6 \text{ cc.}$$

Vapor pressure of water. As a rule gases are measured in the laboratory by collecting them over water in a graduated tube, as represented in Fig. 330. Before the reading is taken the tube A is first raised or lowered until the level of the water is the same within and without the tube; the inclosed gas is then under atmospheric pressure. But to some extent water has evaporated into the tube, and a part of the volume inclosed *is due to water vapor* and not to the gas. If the water vapor could be removed, the gas would occupy a smaller volume. The downward pressure upon the water in the tube A is partly due to the pressure exerted by the gas (say, oxygen) and partly to the pressure exerted by the water vapor. If we could find out how much pressure the water vapor exerts upon the surface of the water within the tube and subtract this from the atmospheric pressure, we should have the pressure which the gas itself exerts at the volume which it occupies. The pressure due to the water vapor is called the *vapor pressure of water*. It in-

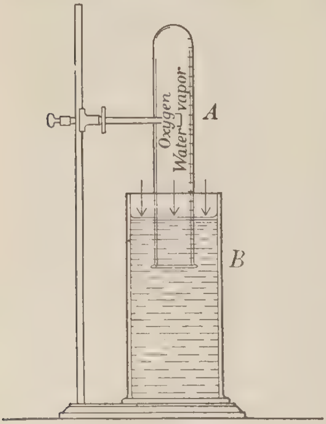


FIG. 330. Measuring the volume of a gas collected over water

creases steadily as the temperature rises, and the table in Appendix E gives its value over the usual range of temperature that occurs in the laboratory.

Solution of problems involving calculation of volumes of gases collected over water. By referring to Fig. 330 it is evident that the atmosphere pressing down upon the surface of the water in the cylinder B tends to force the water up in the tube A and so compresses the gas in the tube. The aqueous vapor mixed with the gas within the tube tends to push the water down and thus acts in opposition to the atmospheric pressure. It is evident, therefore, that to obtain the value of the pressure to which *the gas* in the tube is subjected, we must subtract the value of the vapor pressure of water from the value of the pressure indicated by the barometer. The following example will make this clear:

A gas measured over water has a volume of 300 cc. when the barometer reads 740 mm. and the thermometer 20°. Calculate the volume which the gas will occupy if the pressure is increased to 760 mm., the temperature remaining constant. The effective pressure *on the gas* equals 740 mm. less the vapor pressure of water at 20°, which is 17.53 mm. (Appendix E);

$$740 - 17.53 = 722.47 \text{ mm.}$$

Substituting these values in the equation expressing Boyle's law, we have

$$V \times 760 = 722.47 \times 300, \quad \text{or} \quad V = 285 \text{ cc.}$$

D. TABLE OF SOLUBILITIES

TABLE OF SOLUBILITIES OF SOME OF THE COMPOUNDS OF THE METALS

	Acetate	Bromide	Carbonate	Chlorate	Chloride	Chromate	Hydroxide	Iodide	Nitrate	Oxide	Phosphate	Silicate (ortho)	Sulfate	Sulfide
Aluminum	W	W		W	W		A	W	W	A	A	A	W	A
Ammonium . . .	W	W	W	W	W	W	W	W	W		W		W	W
Barium	W	W	A	W	W	A	W	W	W	A	A	A	I	W
Calcium	W	W	A	W	W	X	W	W	W	X	A	A	X	X
Cobalt	W	W	A	W	W	A	A	W	W	A	A	A	W	A
Copper	W	W	A	W	W	W	A	W	W	A	A	A	W	A
Ferric	W	W		W	W	W	A	W	W	A	A	A	W	A
Ferrous	W	W	A	W	W		A	W	W	A	A	A	W	A
Lead	W	X	A	W	X	A	A	X	W	A	A	A	I	A
Magnesium . . .	W	W	A	W	W	W	A	W	W	A	A	A	W	A
Manganese . . .	W	W	A	W	W	W	A	W	W	A	A	A	W	A
Mercuric	W	W	A	W	W	X		A	W	A	A		X	I
Mercurous	W	A		W	A	A		A	W	A	A		X	
Nickel	W	W	A	W	W	A	A	W	W	A	A	A	W	A
Potassium	W	W	W	W	W	W	W	W	W	W	W	W	W	W
Silver	W	I	A	W	I	A		I	W	A	A		X	A
Sodium	W	W	W	W	W	W	W	W	W	W	W	W	W	W
Stannous	W	W			W	A	A	W		A	A		W	A
Zinc	W	W	A	W	W	W	A	W	W	A	A	A	W	A

W, soluble in water.
A, insoluble in water, soluble in either HCl or HNO_3 or in both.
I, insoluble in water and in acids.
X, slightly soluble in water and slightly or readily soluble in acids.

E. TABLES

DENSITIES AND MELTING POINTS OF SOME COMMON ELEMENTS

Name	Density	Melting Point	Name	Density	Melting Point
Aluminum	2.702	660°	Manganese	7.2	1260°
Antimony	6.684	630.5°	Mercury	13.546	− 38.87°
Arsenic	5.7	——	Nickel	8.9	1452°
Bismuth	9.8	271°	Phosphorus	1.82	44.1°
Calcium	1.55	810°	Platinum	21.45	1755°
Carbon (diamond)	3.51	——	Potassium	0.86	62.3°
Carbon (graphite)	2.25	3500°	Radium	5 (?)	960° (?)
Chromium	7.1	1615°	Silicon	2.4	1420°
Cobalt	8.9	1480°	Silver	10.5	960.5°
Copper	8.92	1083°	Sodium	0.97	97.5°
Gold	19.3	1063°	Sulfur (rhombic)	2.07	112.8°
Iron	7.86	1535°	Tin	7.31	231.8°
Lead	11.34	327.5°	Tungsten	19.3	3370°
Magnesium	1.74	651°	Zinc	7.14	419.4°

TABLE OF SOLUBILITY OF VARIOUS SOLIDS

SUBSTANCE	FORMULA	WEIGHT DISSOLVED BY 100 G. OF WATER AT		
		0°	20°	100°
Calcium chloride	$CaCl_2$	59.5 g.	74.5 g.	159.0 g.
Sodium chloride	$NaCl$	35.70 g.	36.0 g.	39.80 g.
Potassium nitrate	KNO_3	13.30 g.	31.6 g.	246.0 g.
Copper sulfate	$CuSO_4$	14.30 g.	20.7 g.	75.4 g.
Calcium sulfate	$CaSO_4$	0.759 g.	0.203 g.	0.162 g.
Calcium hydroxide	$Ca(OH)_2$	0.185 g.	0.165 g.	0.077 g.

PRESSURE OF AQUEOUS VAPOR EXPRESSED IN MILLIMETERS OF MERCURY

Temperature	Pressure	Temperature	Pressure
15°	12.78	21°	18.65
16°	13.63	22°	19.83
17°	14.53	23°	21.07
18°	15.48	24°	22.38
19°	16.48	25°	23.76
20°	17.53	100°	760.00

F. REFERENCE TABLES

[For convenience these tables also appear facing the inside back cover]

WEIGHT IN GRAMS OF 1 LITER OF VARIOUS GASES UNDER STANDARD CONDITIONS, AND BOILING POINTS UNDER 760-MILLIMETER PRESSURE

Name	Weight of 1 Liter	Boiling Point	Name	Weight of 1 Liter	Boiling Point
Acetylene . . .	1.1621	−83.6°	Hydrogen chloride	1.6398	−85.0°
Air	1.2930		Hydrogen sulfide	1.5392	−59.6°
Ammonia . .	0.7708	−33.3°	Methane	0.7168	−161.4°
Argon.	1.7824	−185.7°	Nitric oxide. . .	1.3402	−151.0°
Carbon dioxide.	1.9768	*	Nitrogen	1.2506	−195.8°
Carbon monoxide	1.2504	−192.0°	Nitrous oxide . .	1.9777	−89.5°
Chlorine . . .	3.214	−34.6°	Oxygen	1.4290	−183.0°
Helium	0.1785	−268.9°	Sulfur dioxide . .	2.9266	−10.0°
Hydrogen . . .	0.08987	−252.7°			

ELECTROCHEMICAL SERIES

1. Lithium
2. Potassium
3. Sodium
4. Calcium
5. Magnesium
6. Aluminum
7. Manganese
8. Zinc
9. Chromium
10. Iron
11. Cadmium
12. Cobalt
13. Nickel
14. Lead
15. Tin
16. Hydrogen
17. Copper
18. Antimony
19. Bismuth
20. Arsenic
21. Mercury
22. Silver
23. Platinum
24. Gold

RELATION BETWEEN ENGLISH AND METRIC CONSTANTS

1 pound (troy) = 373.24 grams
1 ounce (troy) = 31.10348 grams
1 pound (avoirdupois) = 453.59 grams
1 ounce (avoirdupois) = 28.3495 grams
1 kilogram = 2.67923 pounds (troy)
1 kilogram = 2.20462 pounds (avoirdupois)
1 liter = 1.05668 United States liquid quarts
1 gallon = 3.78543 liters
1 cubic centimeter = 0.0610 cubic inch
1 cubic inch = 16.3872 cubic centimeters
1 cubic foot = 28,320 cubic centimeters
1 centimeter = 0.3937 inch
1 meter = 39.37 inches

1 cc. of water at its temperature of greatest density (4° C.) weighs approximately 1 g. For all ordinary purposes, therefore, 1 cc. of water may be regarded as weighing 1 g.

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* Under a pressure of 1 atmosphere, carbon dioxide vaporizes without melting. If subjected to a pressure of 5.2 atmospheres, it melts at − 56.6°.

INDEX

Abrasive, 324
Absolute scale of temperature, 562
Absolute zero, 226, 562
Acetanilide as a catalyst, 92
Acetates, 391
Acetic acid, 139, 391
Acetone, 355
Acetylene, 354
Acid, 200; and ionization, 213; binary, 205; definition of, 201; definition of, in terms of ions, 214; dibasic, 282; monobasic, 282; naming of, 205; strength of, 215; ternary, 205; tetrabasic, 282; tribasic, 282
Acid anhydrides, 249
Acid salts, 283
Action, chemical, 21; mass, 256
Activated charcoal, 141, 344
Adsorption, 141, 344
Affinity, chemical, 23
Agate, 325; a dry jelly, 346
Agent, catalytic, 36, 92; emulsifying, 345; oxidizing, 59; reducing, 59
Air, 229; analysis of, 230; analysis of nitrogen in, 231; analysis of water vapor in, 231; composition of, 229; composition of, constant, 232; constituents in, essential to life, 230; impure, and ventilation, 233; liquefaction of, Fig. 130; liquid, 233; a mixture, 232; oxygen in, 230; pouring liquid, 62; processes tending to change composition of, 231; water vapor in, 230
"Airs," 32
Alchemist, the, 3, 5
Alchemy, 5; results of, 6
Alcohol, absolute, 385; denatured, 387; ethyl, 385; grain, 385; in automobile radiators, 104; methyl, 384; solidified, 346; tax on, 387; wood, 139, 384
Alcohol problem, 386
Alcohols, 384
Alizarin, 403
Alkali metals, 424
Alkalies, 202
Alkaloids, 383
Allotropic forms, 48
Alloys, nature of, 312; of lead and tin, 527; of metals, 416; steel, 491
Aluminum, 462; compounds of, 466; electrolytic production of, 463; hydrolysis of salts of, 468; properties of, 464; uses of, 464; welding by, 465
Aluminum bronze, 506
Aluminum hydroxide, 468
Aluminum oxide, 466
Aluminum silicate, 333
Aluminum sulfate, 468; purification of water with, 478
Alums, 468
Alundum, 467
Amalgams, 509; dental, 509
American Chemical Society, 16
Amethyst, 325; Oriental, 466
Ammonia, 237; aqua, 239; catalytic oxidation of, 245; commercial preparation of, 238;

composition of, 241; conduct, 240; from coal, 239, 360; laboratory preparation of, 238; liquefaction of, 240; properties, 240; uses, 240
Ammonium, 238, 241; salts of, 434
Ammonium carbonate, 435
Ammonium chloride, 434
Ammonium chloroplatinate, 536
Ammonium hydroxide, 241
Ammonium nitrite, preparation of nitrogen from, 223
Ammonium salts, 242; tests for, 242
Ammonium sulfate, 435
Ammonium sulfides, 435
Amorphous solids, 68
Amorphous substance, melting point of, 69
Analysis, method of, 84
Anhydrides, acid, 249
Anhydrous compounds, 77
Aniline, 402
Aniline dyes, 403
Anions, oxidation of, 494; reduction of, 494
Anode, definition of, 105
Anthracene, 403
Anthracite, 138
Antimony, 311; alloys of, 313
Antimony sulfide, in matches, 310
Apatite, 307
Aqua ammonia, 223, 240
Aqua regia, 246
Aqueous vapor, 564, 567
Argentum, 511
Argols, 393
Argon, 226; in air, 229
Arrhenius, 211; portrait of, 212
Arsenic, 310; compounds of, 311; oxide of, 310, 311; uses of, 311; white, 311
Arsenic acid, 311
Arsenic insecticides, 311
Arsenious acid, 311
Arsenious oxide, 311
Arsine, 311
Artificial gems, 467
Asbestos, 454
Aspirin, 402
Aston, 108, 294; portrait of, Fig. 161
Atmosphere, 229; pressure of, 72
Atomic hydrogen flame, 355
Atomic number, 168, 287; and properties of elements, 288
Atomic structure and valence, 173
Atomic theory, 116
Atomic weights, fractional, 173, 294; relative, 115
Atoms, 26, 109; atomic number of, 168, 287; borrowing, 172; electrical composition of, 166; lending, 172; nucleus of, 167, 287; satellite electrons of, 167; structure of, 165; valence of, 158; of no valence, 170
Automobile casings, Fig. 272
Avogadro, law of, 111; portrait of, Fig. 58
Avogadro's law, 111; applied to problems, 153, 356

Babbitt metal, 313, 527
Bacteria in impure water, 476
Bakelite, 402
Baking, aërating agents in, 469
Baking powders, 470
Balancing equation, 124
Barite, 282, 449
Barium, 449; salts of, 449
Bases, 197, 201; definition of, in terms of ions, 214; and ionization, 214; naming of, 206; strength of, 215
Battery, storage, 525
Bauxite, 463
Becquerel, 547
Beers, 386
Bell metal, 506
Benzene, 402

Benzine, 352
Benzoic acid, 402
Bessemer converter, 488
Bessemer process, acid, 487
Bismuth, 312; action of water on salts of, 312; alloys of, 313
Bismuth oxychloride, 312
Bismuth oxynitrate, 312
Bisque, 335
Bisulfates, 283
Bivalent atoms, 159
Blast furnace, 485
Blast lamp, 59
Bleach, 445
Bleaching, by chlorine, 183; by hydrogen peroxide, 92; by sulfurous acid, 276
Bleaching powder, 180, 445; manufacture of, 446
Blister copper, 505
Block tin, 519
Blowpipe, 367; oxyacetylene, 355; oxyhydrogen, 59
Blue vitriol, 507
Blue-printing, 496
Bluestone, 507
Boiler scale, 454
Boiling point, 71; definition of, 72; and pressure, 72; of solutions, 103; of various gases, 568, facing the inside back cover
Bonds, valence, 161
Bone ash, 307, 448
Boneblack, 140, 142
Borax, 328; in soap, 397
Borax-bead test, 328
Bordeaux mixture, 508
Boric acid, 327
Boric oxide, 328
Bornite, 504
Boron, 327; in glass, 333; in plant growth, 318
Borosilicates, 333
Bottles, making of, 332
Boyle, portrait of, Fig. 38
Boyle's law, 63, 561
Brand, 307
Brandy, 386
Brass, 506
Brazing, 328, 521
Bread-making, chemical changes in, 388
Brick, 334; vitrified, 334
Brimstone, 264
Bromide ions, test for, 302
Bromides, 299, 300
Bromine, 299
Bronze, 506; aluminum, 506; manganese, 506, 539
Bunsen, portrait of, Fig. 124
Bunsen burner, 366
Burning, 6, 38; explanation of, 39; gain in weight during, 39
Butane, 351
Butter, 345
Butter fat, 395
By-product coke ovens, 360
By-products, 188

Cadmium, 452
Caffeine, 384
Calcite, 441
Calcium, 440; sulfides of, 267
Calcium acid carbonate, 441
Calcium acid phosphate, 319
Calcium arsenate, 311
Calcium carbide, 354, 446
Calcium carbonate, 440
Calcium chloride, 448
Calcium cyanamide, 447
Calcium hydroxide, 444
Calcium phosphate, 448
Calcium sulfate, 446
Caliche, 428
Calomel, 510
Calorie, 70; large, 411
Calorific value of fuels, 362
Camphor, 382
Caramel, 374
Carat, 136, 533

Carbides, 142
Carbohydrates, 372; in foods, 406
Carbolic acid, 402
Carboloy, 497
Carbon, amorphous, 138; chemical conduct of, 142; compounds of, 372; crystalline, 136; occurrence of, 135; physical properties of, 141; uses of, 142
Carbon black, 140, 142
Carbon dioxide, 145; decrease of, in air, 232; in air, 229, 231; increase of, in air, 231; liquid, 147; preparation of, 146; properties, 146; solid, 63, 147; test for, 148; uses of, 148
Carbon disulfide, 270
Carbon monoxide, 150; effect on birds, 151; formation of, in automobiles, 151; formation of, in stoves, 151; poisoning by, 151
Carbon tetrachloride, 354; in fire extinguishers, 149
Carbonates, 207
Carbonates, solubility of, 421
Carbonic acid, 148, 207
Carbonic acid gas, 145
Carborundum, 323
Carborundum furnace, 323
Carburetors, 368
Carnallite, 430, 452
Carnotite, 543, 549
Casein, 345, 374; coagulation of, 343
Cassiterite, 519
Cast iron, 485, 486
Castner cell, 195
Catalyst and speed of reaction, 92
Catalysts, 37, 92; positive and negative, 92
Catalytic action, of manganese dioxide, 37; of platinum, 535; of water, 77
Catalytic agents, 36
Cathode, definition of, 105
Cations, oxidation of, 493, 494
Caustic potash, 197
Caustic soda, 196
Cavendish, portrait of, Fig. 27
Caves, formation of, 442
Cell, Castner, 195; Vorce, 180
Cellophane, 380, 381
Celluloid, 382
Cellulose, 378; action of hydrochloric acid on, 378; action of nitric acid on, 381; action of sodium hydroxide on, 381
Cellulose acetate, 381
Cellulose nitrates, 381
Cement, 336
Cement clinker, 336
Cementite, 483
Centigrade scale of temperature, 560
Centrifugals, 373
Cesium, 424
Chalcedony, 325
Chalcocite, 504
Chalcopyrite, 504
Chalk, precipitated, 441
Chamber process for sulfuric acid, 279
Changes, chemical, 21; physical, 22
Charcoal, 139; activated, 141, 344; animal, 140
Charles's law, 64, 563
Cheese, 375
Chemical action, 21
Chemical affinity, 23
Chemical changes, 21
Chemical conduct, 28
Chemical energy, 28
Chemical equations, 124
Chemical industries, 12
Chemical knowledge incomplete, 14
Chemical library, 557
Chemically pure compounds, 188
Chemist, the industrial, 13; work of, 11

Chemistry, and other sciences, 14; definition of, 9; future of, 15; as a profession, 15
Chile saltpeter, 193, 428; iodine in, 301
Chinaware, 334
Chinese wood oil, 527
Chlorauric acid, 534
Chloride ions, tests for, 259, 421
Chloride of lime, 445
Chlorides, solubility of, 421; tests for, 187
Chlorine, 177; action of, on hydrogen, 182; action of, on metals, 181; action of, on water, 182; as a disinfectant, 183; bleaching by, 183; chemical conduct of, 181; electrolytic preparation of, 180; nascent, 246; occurrence of, 178; preparation of, 178; properties of, 181; purification of water by, 183, 477; uses of, 183; valence of, 183
Chlorine family, 297
Chloroform, 354
Chloroplatinic acid, 536
Chromates, 541
Chrome iron ore, 540
Chrome yellow, 526, 541
Chromic acid, 541
Chromic chloride, 541
Chromic hydroxide, 541
Chromic salts, 541
Chromite, 540
Chromium, 540; compounds of, 541; preparation of, by Goldschmidt process, 465
Chromium plating, 542
Cider, 392
Cinnabar, 508, 511
Citric acid, 391
Clay, 334
Clay products, 334
Coagulation of colloidal dispersions, 342
Coal, 138; destructive distillation of, 139; mining of, 139
Coal gas, 360
Coal tar, 360, 399; composition of, 400; derivatives of, 400
Coal-tar compounds, 399
Coal-tar dyes, 403
Cobalt, 496; properties, 497
Cobalt glass, 498
Cobalt nitrate, 498
Cobalt oxide, 498
Cocaine, 384
Coconut oil, 394
Cod-liver oil, 394; vitamins present in, 408
Coinage, gold, 506, 533; nickel, 497, 506; silver, 506
Coke, 138
Coke oven, by-product, 360; beehive, 360
Cold storage plants, 240
Collodion, 381
Colloid, 340
Colloid mill, 341
Colloidal dispersions, 339; coagulation of, 342; preparation of, 341; preserving of, 343; properties of, 342
Colloidal state, 339
Colloids and crystallization, 344
Combination, reactions of, 130
Combining volumes, law of, 111
Combustion, 41; heat of, 43; speed of, 42; spontaneous, 44
Commercial compounds, 188
Compounds, chemically pure, 188; commercial, 188; definition of, 19; illustration of, 20; nonpolar, 172; number of, 25; polar, 170
Concrete, 336; reënforced, 337
Condensation, heat of, 72
Condensite, 402
Conductivity of solutions, 211
Congo red, 402

Conservation, of energy, 28; of matter, 18
Contact process for sulfuric acid, 278
Cooper-Hewitt lamp, 509
Copper, 503; action of nitric acid on, 246; action of sulfuric acid on, 280; blister, 505; chemical conduct of, 505; electrolytic refining of, 505; hardening of, 519; metallurgy of, 505; occurrence of, 503; properties, 503; uses, 506
Copperas, 282, 492
Coral, 441
Corn, composition of, 25
Corn oil, 394
Corn sirup, 376
Cornstalks, uses of, 378
Corrosive sublimate, 510
Corundum, 463, 466
Cotton, mercerized, 381
Cotton fiber, 379
Cottonseed oil, 394; decolorizing of, 344; hydrogenation of, 396
Cottrell method for settling dust particles, 346
Cracking of oils, 352
Cream of tartar, 393
Cresylic acid, 345, 402
Cryolite, 298, 463
Crystals, 68; formation of, from solution, 218; structure of, 218
Cullinan diamond, 136
Cupric compounds, 507
Cupric ion, tests for, 508
Cupric oxide, 507
Cupric sulfate, 507
Cupric sulfide, 508
Cuprite, 504
Cuprous compounds, 507
Cuprous oxide, 507
Curie, Madame, 547; portrait of, Fig. 325
Curie, Pierre, 548
Cyanamide, 446, 448
Cyanogen, 250

Dalton, 116; portrait of, Fig. 57
Davy, 193, 368; portrait of, Fig. 110
Decomposition, reactions of, 130
Definite composition, law of, 90
Definite proportion, law of, 90
Dehydrating agent, 281
Deliquescence, 104
Denaturants, 387
Denatured alcohol, 387
Density, definition of, 81; of each of some common elements, 567
Developer, photographic, 515
Dewar flask, 234
Dextrin, 378
Dextrose, 374, 376; produced from cellulose, 378
Diamond, 136; artificial, 137; Cullinan, 136
Diastase, 386, 387
Dibasic acids, 282
Disinfectant, chlorine as a, 183; cresylic acid as a, 402
Displacement series, 216
Distillation, 79; destructive, 139; fractional, 353; of water, 79
Dolomite, 453
Double replacement, reactions of, 131
Driers for paints, 527
Dry ice, 63, 148
Duralumin, 464
Duriron, 491
Dyeing, 471
Dyes, 471; aniline, 403; coal-tar, 403; synthesis of first, 13; vegetable, 403
Dynamite, 399

Earth's crust, composition of, 24
Effervescence, 102
Efflorescence, 104

Electric furnaces, 369
Electric toaster, 540
Electricity, negative, 165; positive, 165
Electrochemical industries, 419
Electrochemical series, 216, 568, facing the inside back cover; of halogens, 301
Electrode, definition of, 105
Electrolysis, 104, 210; definition of, 104; and ionization, 213; of fused salts, 218; of water, 35
Electrolyte, a polar compound, 211
Electrolytes, 104, 210
Electron, 166
Electrons, binding, 167; from radium, 550; loss or gain of, 170; satellite, 167, 287; shared, 172; valence, 173
Electroplating, with chromium, 542; with nickel, 497; with silver, 512
Electroscope, 548
Electrothermal metallurgy of steel, 490
Electrotyping, 507
Elementary substances, 19
Elements, atomic numbers of, 168; classification of, 286; definition of, 19; illustration of, 20; in earth's crust, 24; in living things, 25; molecular weight of, 115; names of, 26; native, 26; occurrence of, 25; of the Greeks, 4; periodic arrangement of, 289; predicted by periodic law, 292; relative abundance of, 24; symbols of, 26; table of, inside back cover; valence of, 162; with different atomic weights, 293
Emery, 463, 466
Emulsifying agent, 345
Emulsions, 344
Enamels, 335
Energy, 28; chemical, 28; law of conservation of, 28
Energy value of foods, 409
Enzymes, 387
Epsom salts, 282, 453
Equations, 27; balanced, 124; balancing of, 124; chemical, 124; formula, 124; problems based on, 126; various meanings of, 129; word, 124
Equilibrium, 256; at saturation, 98; illustration of, at saturation, 98; in solution, 257
Ester, 394
Ethane, 351
Ether, 385
Ethyl gasoline, 300
Ethylene bromide, 300
Ethylene glycol, 387
Eudiometer, 85
Evaporation, 71
Explosions, 367; causes of, 43; mine, 368; results of, 43
Explosive mixtures, 367

Families, periodic, 291
Fats in foods, 406
Feldspar, 327
Fermentation, acetic, 392; alcoholic, 386; cause of, 375; lactic, 375
Ferric alum, 493
Ferric chloride, 493
Ferric hydroxide, 494
Ferric ion, tests for, 495
Ferric oxide, 495
Ferric salts, 492; reduction of, 494
Ferric sulfate, 493
Ferrochromium, 491, 540
Ferromanganese, 491, 538
Ferrotitanium, 543
Ferrotungsten, 544
Ferrous hydroxide, 494
Ferrous ion, test for, 496
Ferrous salts, 492; oxidation of, 493

Ferrous sulfate, 492; purification of water with, 478
Ferrous sulfide, 492
Ferrovanadium, 543
Fertilizers, 317; constituents of, 318; sources of, 318
Film, photographic, 514
Filters, slow sand, 477
Fire, 38
Fire damp, 354
Fire extinguishers, foam, 469; portable, 149
Fixation of nitrogen, 448; by plants, 224
Flame, atomic hydrogen, 355
Flame reaction, 435
Flame test, 435
Flames, 364; conditions necessary for, 364; cones in, 365; oxidizing, 366; reducing, 366; structure of, 365
Flare, magnesium, 452
Flashlight, 452
Flint, 325
Flotation, 418
Flowers of sulfur, 264
Fluorine, 297
Fluorite, 298
Flux, 485
Foam fire extinguishers, 469
Foams, 347
Fogs, 347
Foods, 406; amount necessary for health, 411; balanced ration of, 413; energy value of, 409; fuel value of, 411; function of, 408, 409; preservation of, 388; preservatives in, 389; sterilized, 388; table of composition of, 410
Fool's gold, 495
Formaldehyde, 385
Formalin, 385
Formic acid, 150
Formulas, 27; and molecular weights, 121; how obtained, 121; of salts, 204; percentage composition from, 123; represent molecules, 120; simplest, 123; steps in determination of, 123; structural, 162
Fractional atomic weights, 173
Fractional distillation, 353
Franklinite, 456
Frary metal, 527
Frasch extraction of sulfur, 263
Freezing point, 68; of solutions, 103
Fuel gases, composition of, 362
Fuel oil, 352
Fuels, calorific value of, 362; heat values of, 362; liquid, 359; solid, 359; solid, calorific value of, 363
Fuller's earth, 344
Furnaces, arc, 369; blast, 485; electric, 369; open-hearth, 488; resistance, 369; reverberatory, 489; smoke-consuming, 364
Fusion, heat of, 70

Galenite, 523
Galvanized iron, 456
Gas, heat changes during compression or expansion, 66; volume change of, with pressure, 63; volume change of, with temperature, 64
Gas mask, 142
Gas volumes, reduction of, to standard conditions, 561
Gases, changing of, to liquids, 72; kinetic theory of, 67; liter density of, 82; molecular weight of, 113; variation in volume of, 45
Gasoline, 352; casing-head, 344; fire from, 353
Gay-Lussac, law of, 111; portrait of, Fig. 56
Gel, 346

Gems, artificial, 467
German silver, 506
Glass, 331; blowing of, 331; colloidal color of, 342; color of, 333; etching of, 299; frosting of, 299; molding of, 331; optical, 333; plate, 332; pyrex, 333; varieties of, 333; window, 332
Glauber's salt, 426
Glucose, 376
Glycerin, 397, 398
Glycerin nitrate, 398
Glycerol, 397
Glyceryl radical, 394
Glycol, 387
Gold, 532; chemical conduct of, 534; colloidal, 341; extraction, 534; fool's, 495; in photography, 515; in ruby glass, 333; occurrence, 533; properties of, 532; the standard of value, 533; white, 533
Gold coinage, 533
Goldschmidt, reduction process, 464
Gram-atomic weights, 125
Gram-molecular weights, 125
Granite, 327
Granite ware, 335
Graphite, 137; artificial, 138
Grease spots, removal of, 499
Green vitriol, 492
Grouping, periodic, 287
Groups, periodic, 288
Gunpowder, 433
Gypsum, 282, 446

Haber process, 238, 255
Hall, 462; statue of, Fig. 5
Halogens, 297; electrochemical series of, 301; properties of, contrasted, 303
Hard waters, composition of, 478; softening of, 479
Heat, changes of, during melting and freezing, 70; unit of, 70
Heat of combustion, 43
Heat of condensation, 72
Heat of fusion, 70
Heat of solidification, 70
Heat of vaporization, 72
Heavy spar, 449
Helium, 225; occurrence of, 225; in air, 229
Helium atoms from radium, 551
Helium-filled dirigible, Fig. 125
Hematite, 484
Henry's law, 101
Heptane, 351
Hexane, 351
High-school laboratory, 15
Honey, 344, 376
Hopkins, 293; portrait of, Fig. 164
Human body, composition of, 25
Humus, 317
Hydrates, definition of, 77
Hydraulic mining, 534
Hydriodic acid, 301
Hydrobromic acid, 300
Hydrocarbons, 350
Hydrochloric acid, 185, 186; properties of, 186; tests for, 187
Hydrocyanic acid, 250
Hydrofluoric acid, 298; action of, on glass, 298
Hydrogen, 51; a measure of valence, 159; chemical conduct of, 56; discovery of, 52; occurrence of, 51; physical properties of, 56; preparation of, from acids, 54; preparation of, from water, 53
Hydrogen-arc welding torch, 356
Hydrogen bromide, 300
Hydrogen chloride, 185
Hydrogen cyanide, 250
Hydrogen fluoride, 298
Hydrogen iodide, 301
Hydrogen nitrate, 242

Hydrogen peroxide, 90
Hydrogen sulfide, 267; acid properties of, 268; action of, on metals, 269; oxidation of, 268; reducing action of, 268
Hydrogenation of oils, 396
Hydrolysis of salts, 429
Hydrosulfuric acid, 268; salts of, 269
Hydroxides, 206; solubility of, 421
Hydroxyl radical, 203
Hygroscopic bodies, 104

Ice, dry, 148; manufacture of, 240
Iceland spar, 441
Ilmenite, 543
Indicators, 203
Indigo, 403
Industries, chemical, 12
Infusorial earth, 325
Ink, printer's, 142
Ink stains, removal of, 499
Inks, 344, 499
Insecticides, 508; arsenic, 311; carbon disulfide, 270; lime-sulfur spray, 267; prussic acid, 250
Insoluble salts, 420
Iodide ions, test for, 302
Iodides, 301
Iodine, 300; and goiter, 301; in Chile saltpeter, 301; in thyroid gland, 301; tincture of, 301; action of, on starch, 302
Iodoform, 354
Ionic oxidation, 493
Ionic reduction, 494
Ionic tests, 421
Ionization, 210; and acids, 213; and bases, 214; and electrolysis, 213; and electrolysis of water, 215; and neutralization, 214; and salts, 214; percentage of, 212; representation of, 211; theory of, 211
Ions, 211; and atoms, 212
Iridium, 545
Iron, 482; action of, on steam, 54; cast, 485, 486; compounds of, 492; galvanized, 456; occurrence of, 483; pure, 483; rusting of, 495; valence of, 492; wrought, 487
Iron carbide, 483
Iron disulfide, 495
Iron of commerce, 483
Iron ore, 484
Isomeric compounds, 374
Isotopes, 294

Jasper, 325
Jellies, 345

Kaolin, 327, 333
Kelp, 301
Kerosene, 352
Kindling temperature, 44
Kinetic theory of gases, 67
Krypton, 226; in air, 229

Lacquers, 381, 529
Lactic acid, 375
Lactose, 374
Lakes, 472, 528
Lamp, blast, 59; Cooper-Hewitt, 509; miner's, 368; safety, 368
Lampblack, 140
Langmuir, 108, 355; portrait of, Fig. 162
Latent image, 515
Latex, rubber, 458
Laughing gas, 248
Lavoisier, 38; portrait of, Fig. 20
Law, of Avogadro, 111, 153, 356; of Boyle, 63, 561; of Charles, 64, 563; of combining volumes, 111; of conservation of energy, 28; of conservation of matter, 18; of definite composition, 90; of Gay-Lussac, 111; of Henry, 101; of multiple proportion, 93; periodic, 290

Lazy elements, 224
Lead, 523; alloys of, 527; chemical conduct of, 523; compounds of, 524; isotope of, from radium, 552; metallurgy of, 523; occurrence of, 523; oxides of, 524; poisoning by, 524; red, 525; uses of, 524; valence of, 524
Lead acetate, 391, 526
Lead arsenate, 311
Lead buckles, 526
Lead carbonate, 526; basic, 526
Lead chloride, 526
Lead chromate, 526, 541
Lead nitrate, 526
Lead peroxide, 525
Lead poisoning, 524
Lead sulfate, 526
Lead sulfide, 524
Leather, artificial, 381
Leblanc method for soda, 427
Levulose, 374, 376
Lewis, portrait of, Fig. 163
Library, chemical, 557
Lime, 443; air-slaked, 444; chloride of, 445; hydrated, 444; slaked, 444
Limekiln, 443, 444
Limestone, 440
Lime-sulfur spray, 267
Limewater, 148, 444
Limonite, 484
Linseed oil, 527
Liquefaction of air, 234, Figs. 130, 131
Liquids, freezing point of, 68; melting point of, 68; miscible, 100; molecular weight of, 114; nature of, 68; undercooled, 69
Liter-density of gases, 82
Litharge, 525
Lithium, 424; isotopes of, 294
Lithopone, 457
Litmus, 187, 203
Lubricating oil, 352
Lunar caustic, 513
Lye, 196

Magnalium, 452, 464
Magnesite, 453
Magnesium, 452
Magnesium carbonate, 453
Magnesium silicates, 453
Magnesium sulfate, 453
Magnetism, 23
Magnetite, 484
Malt, 386
Maltose, 386
Manganese, 538; in plant growth, 318
Manganese bronze, 506, 539
Manganese dioxide, 538; in preparation of chlorine, 178; in preparation of oxygen, 36
Manganin, 539
Manganous sulfate, 539
Marble, 441
Marsh gas, 353
Mass action, 256
Matches, 309
Matter, allotropic forms of, 48; composition of, 174; conservation of, 18; definition of, 18; forms of, 18; states of, 62
Mayonnaise, 345
Melting point, 68; of each of some common elements, 567
Mendeléeff, 287; portrait of, Fig. 158
Mercuric chloride, 510
Mercuric compounds, 510
Mercuric oxide, 510; decomposition of, 21, 33; derivation of formula of, 122; preparation of oxygen from, 34
Mercuric sulfide, 511
Mercurous chloride, 510
Mercurous compounds, 510
Mercury, 508; chemical conduct of, 509; compounds of, 510; metallurgy of, 509; uses of, 509

Metallurgy, 418
Metals, 415; action of nitric acid on, 245; alloys of, 416; chemistry of, 415; compounds of, 419; definition of, 416; noble, 416; primitive, 3; properties of, 415; the alkali, 424; transmutation of, 4
Metasilicic acid, 326
Methane, 351, 353; alcohol derived from, 384
Methane series, 351
Methanol, 139, 384
Method, scientific, 116
Metric system, relation between English and metric constants, 568, facing the inside back cover
Mica, 326
Milk, 345
Mine explosions, 368
Mineral matter, in foods, 406; in water, 78
Minium, 525
Miscible liquids, 100
Mixtures, explosive, 367; definition of, 20; illustration of, 20
Moissan, 137, 298
Molasses, 373
Molecular weights, actual, 110; from weight of 22.4 liters, 113; of elements, 115; of gases, 113; of liquids, 114; of solids, 114; relative, 112; represented by formulas, 121; standard for, 112
Molecules, 108; formulas of, 121; size of, 108
Molecules and atoms, distinction between, 109
Molybdenum, 544
Monel metal, 497, 506
Monobasic acids, 282
Mordants, 472
Morley, 89; portrait of, Fig. 49
Morphine, 384
Mortar, 336, 445
Moseley, 287; portrait of, Fig. 159
Moth balls, 402
Movie films, 381
Multiple proportion, law of, 93
Muriatic acid, 186
Muscle Shoals, Fig. 131

Naphtha, 352; in soap, 397
Naphthalene, 402
Nascent chlorine, 246
Nascent state, 184
Natural gas, 362
Neon, 226, 295; in air, 229
Neutralization, 202; and ionization, 214; definition of, in terms of theory of ionization, 214
Nichrome, 540
Nickel, 496; as a catalyst, 396; electroplating with, 497; properties of, 497
Nickel sulfate, 498
Nicotine, 384
Nitrates, 247; solubility of, 421; test for, 247
Nitric acid, 242; acid properties of, 245; action of, on metals, 245; oxidizing action of, 245; preparation of, from air, 244; preparation of, from nitrates, 243; salts of, 247; uses of, 247
Nitric oxide, 249
Nitrifying bacteria, 224
Nitrobenzene, 402
Nitrocellulose, 381
Nitrocellulose film, 514
Nitrogen, 221; acids of, 242; chemical conduct of, 223; compounds of, with carbon, 250; fixation of, 224, 448; in air, 231; oxides of, 248; preparation of, from air, 222; preparation of, from compounds, 223; uses of, 223; utilization of atmospheric, 320
Nitrogen dioxide, 249

Nitrogen fixation, 448
Nitrogen pentoxide, 249
Nitrogen trioxide, 249
Nitrogenous matter in fertilizers, 318
Nitroglycerin, 399
Nitrous acid, 247
Nitrous oxide, 248
Noble metals, 416
Nonelectrolytes, 104
Nonpolar compounds, 172
Normal salts, 282
Nucleus, charge of, 168
Nucleus of atoms, 166, 167, 287
Nutrients, 406

Octane, 351
Oil, Chinese wood, 527; drying, 527; fuel, 352; linseed, 527; lubricating, 352
Oil dag, 343
Oil of vitriol, 277
Oil wells, 350
Oils, animal, 394; cracking of, 352; changing of, to solid fats, 396; hydrogenation of, 396; vegetable, 394
Oleic acid, 393
Olein, 394; changing of, into stearin, 396
Oleomargarine, 395
Olive oil, 394
Onyx, 325
Opal, 325; a partially dry jelly, 346
Open-hearth process, basic, 488
Orbits, completed, 170; of electrons, 168
Ore, 418
Ores, concentration of, 418; flotation of, 418; roasting of, 418
Organic acids, 391
Organic compounds, 372
Orthosilicic acid, 326
Oxidation, 41; heat of, 43; in broad sense, 493, 494; products of, 41
Oxides, 41; definition of, 42
Oxides of nitrogen, 248
Oxidizing agent, 59
Oxyacetylene blowpipe, 355
Oxygen, 32; analysis of, in air, 230; chemical conduct of, 37; discovery of, 33; discovery of, by Scheele, 177; importance of, 44; occurrence of, 33; physical properties of, 37; preparation of, from mercuric oxide, 34; preparation of, from potassium chlorate, 36; preparation of, from water, 35; relation of, to ozone, 47
Oxygen helmet, 46
Oxyhydrogen blowpipe, 59
Ozone, 46; relation of, to oxygen, 47

Paints, 527
Palladium, 535, 545
Palm oil, 394
Palmitic acid, 393
Palmitin, 394
Paper, 379
Paper pulp, 379
Paraffin, 352
Paris green, 311
Parkes process, 523; for silver, 513
Pasteur, 375; portrait of, Fig. 219
Pasteurized milk, 375
Pearls, 441
Pectin, 346
Pentane, 351
Percentage composition from formulas, 123
Periodic arrangement of elements, 289
Periodic groups, 288; two families in, 291
Periodic law, 286; imperfection of, 293; statement of, 290; value of, 292
Perkin, 13; portrait of, Fig. 6

Permanent hardness, 479
Permanganic acid, 539
Petroleum, 350; composition of, 350; first use of, 350; refining of, 351
Pewter, 521, 527
Phenol, 402
Philosopher's stone, 6, 307
Phlogiston, 6
Phosphate rock, mining of, 319
Phosphates, 309; in fertilization, 318; solubility of, 421
Phosphorescence, 308, 547
Phosphoric acid, 309; salts of, 309
Phosphoric anhydride, 308
Phosphorite, 307
Phosphorus, 306; action of, on air, 222; chemical conduct of, 308; oxides of, 308; preparation of, 308; red, 306; sulfides of, 308; uses of, 309; white, 306; yellow, 306
Phosphorus family, 306
Phosphorus pentoxide, 308
Phosphorus sesquisulfide, 308
Phosphorus trioxide, 308
Photographic developer, 515
Photographic films, 346, 381, 514
Photographic negative, 514
Photographic positive print, 515
Photographic proofs, 515
Photographic toning, 515
Photography, 514
Physical changes, 22
Picric acid, 402
Pigments, in paints, 528; in glazes, 335
Pitch, 403
Pitchblende, 548, 549
Placer mining, 534
Plaster, 445
Plaster of Paris, 446
Platinized asbestos, 535
Platinum, 534; as a catalyst, 535; as a catalyst for oxidation of ammonia, 245; as a catalyst for sulfur trioxide, 277; chemical conduct of, 535; colloidal, 341; in photography, 515; occurrence of, 534; placer mining of, 535; uses of, 536
Plumbum, 523
Polar compounds, 170, 211
Porcelain, 334
Portland cement, 336
Potash, caustic, 197
Potassium, 192; chemical action of, 195; compounds of, 430; discovery of, 192; occurrence of, 193; preparation of, 194; properties of, 195; radioactive, 553; valence of, 196
Potassium bisulfate, 432
Potassium bromide, 432
Potassium carbonate, 432
Potassium chlorate, 431; preparation of oxygen from, 36
Potassium chloride, 432
Potassium chloroplatinate, 536
Potassium compounds in fertilizers, 319
Potassium dichromate, 541; oxidizing action of, 542
Potassium ferricyanide, 496
Potassium ferrocyanide, 495
Potassium hydroxide, 197; chemical conduct of, 197
Potassium iodide, 301, 432
Potassium nitrate, 432
Potassium permanganate, 539; oxidizing properties of, 539
Potassium salts, source of, in the United States, 432
Potassium sulfate, 432
Pottery, decoration of, 335; glaze of, 335; white, 334
Powder, baking, 470
Precipitate, representation of, 131
Preservatives in food, 389
Pressure, standard, 65, 561

Pressure and solubility, 101
Priestley, 32; portrait of, Fig. 14
Producer gas, 361
Propane, 351
Properties, physical, 28
Properties of elements, and atomic number, 288
Proteins, 406
Proton, 165; arrangement in nucleus of atom, 167
Prussian blue, 495
Prussiate of potash, red, 496; yellow, 495
Prussic acid, 250
Ptyalin, 388
Puddling furnace, 487
Pure Food and Drugs Act, 413
Putrefaction of food, 388
Pyrite, 495
Pyrolusite, 538
Pyrrhotite, 492

Quadrivalent atoms, 159
Qualitative analysis, 421
Quartz, 324; varieties of, 325; vessels of, 325
Quartz mining, 534
Quick lime, 443
Quinine, 384

Radiators, alcohol in, 103; glycol in, 387
Radical, ammonium, 238, 241
Radicals, 203; formula of molecules containing, 204; valence of, 204
Radioactive elements, 551
Radioactive thorium, 554
Radioactivity, 548
Radiograph, 548
Radium, discovery of, 547; disintegration of, 550; energy of, 552; half-life period of, 550; importance of, 552; physiological effects of, 553; practical uses of, 553; production of, 549; properties of, 548; quantity of, available, 549; source of, 551; value of, 549
Radon, 552
Ramsay, Sir William, 224; portrait of, Fig. 123
Rasorite, 327
Ration, balanced, 413
Rayon, 380
Rays, alpha, 550; beta, 550; gamma, 550; nature of radioactive, 550; X, 547
Reactions, completion of, by escape of a gas, 258; completion of, by formation of un-ionized molecules, 259; completion of, by precipitation, 258; conditions of, not shown in equation, 130; flame, 435; ionic, 215; of combination, 130; of decomposition, 130; of double replacement, 131; of simple replacement, 131; reversible, 255; types of, 130
Rectifier, electrical, 509
Red lead, 525
Reducing agent, 58, 59
Reduction, 58; Goldschmidt process, 464; in broad sense, 494; ionic, 493
Reënforced concrete, 337
Refrigerators, use of ammonia in, 274; use of sulfur dioxide in, 275
Relative atomic weights, 115
Relative molecular weights, 112
Relative values, meaning of, 110
Rennet, 375
Resins, 528
Respiration, chemical changes during, 231
Reverberatory furnace, 489
Reversible reactions, 255; completion of, 257
Roasting of ores, 418

Roll sulfur, 264
Röntgen radiation, 547
Rose metal, 527
Rubber, 457; accelerators for, 459; coagulation of, 343; composition of, 458; fillers for, 459; vulcanizing of, 459
Rubber latex, 458
Rubidium, 424
Ruby, 466
Rusting of iron, 495
Rutile, 543

Saccharine, 402
Salad oils, 395
Sal ammoniac, 434
Sal soda, 426, 428
Salicylic acid, 402
Salt, common, 425
Salt brine, 425
Saltpeter, 221, 432; Chile, 193, 221
Salts, 202; acid, 283; definition of, 202; definition of, in terms of ions, 214; formulas of, 204; hydrolysis of, 429; and ionization, 214; naming of, 206; normal, 282; number of, 203; precipitation of, 420; preparation of insoluble, 420; preparation of soluble, 420; solubility of, 420; Stassfurt, 430
Sand, 325
Sand filters, rapid, 478; slow, 477
Sandstone, 325
Sapphire, 466
Satellite electrons, 167, 287; arrangement of, 168
Saturated solutions, 98
Scale, boiler, 454
Scales of temperature, comparison of, 563
Scheele, 177; portrait of, Fig. 97
Scheele's green, 311
Science, definition of, 16
Scientific method, 116
Searles Lake, 327, 433
Selenium, 545; in glass, 333
Series, electrochemical, 216; page facing inside back cover
Setting, of casein, 375; of cement, 336; of mortar, 445; of plaster of Paris, 446
Sewage-disposal plant, 45
Shells, 441
Siderite, 484
Silica, 323, 324; absorption of, by plants, 323; action of hydrofluoric acid on, 298
Silicate industries, 331
Silicates, 326; aluminum, 333; solubility of, 421
Silicic acids, 326; condensed, 327; salts of, 326
Silicides, 323
Silicon, 322; acids of, 326; occurrence of, in nature, 323; preparation of, 322
Silicon carbide, 323
Silicon dioxide, 323, 324; properties of, 325
Silk, 345; artificial, 380; natural, 380
Silk fiber, 379
Silver, 511; chemical conduct of, 511; colloidal, 341; compounds of, 513; electroplating with, 512; German, 497, 506; metallurgy of, 513; sterling, 512; uses of, 512
Silver bromide, 300, 513
Silver chloride, 513
Silver halides, 513
Silver iodide, 301, 513
Simple replacement, reaction of, 131
Slag, 485
Slags as fertilizers, 319
Smalt, 498
Smithsonite, 456
Smoke, prevention of, 363

Smokeless powder, 381
Smokes, 346
Soap, cleansing property of, 398; coagulation of, 343, 397; insoluble, 398; manufacture of, Fig. 237; a partially dry jelly, 346; scouring, 325; soft, 397; varieties of, 397
Soaps, 396
Soapstone, 454
Soda, 426; baking, 426; caustic, 196; washing, 426, 428
Soda water, effervescence of, 102
Sodium, 192; action of, on water, 53; chemical action of, 195; discovery of, 192; occurrence of, 193; preparation of, 194; properties of, 192; valence of, 196
Sodium benzoate, 402; in foods, 389
Sodium bicarbonate, 428
Sodium bisulfate, 283
Sodium bromide, 429
Sodium carbonate, 426
Sodium chloride, 425
Sodium cyanide, 251, 429
Sodium dichromate, 541
Sodium ferrocyanide, 495
Sodium hydrogen carbonate, 428
Sodium hydrogen sulfate, 243
Sodium hydroxide, 196; chemical properties of, 197; from electrolysis of salt, 181; preparation of, 197
Sodium hyposulfite, 429
Sodium iodide, 429
Sodium nitrate, 428
Sodium nitrite, 247
Sodium phosphate, 309
Sodium sulfate, 426
Sodium tetraborate, 328
Sodium thiosulfate, 428
Soft soap, 397
Soft solder, 521
Softening of water, 479; zeolite process for, 480
Soils, 316; acidity of, 317; formation of, 316; liming of, 317; varieties of, 316
Solder, 527; soft, 521
Soldering, 521
Solidification, heat of, 70
Solids, crystalline, 68; molecular weight of, 114, 218; nature of, 68
Solubility, conditions affecting, 100; definition of, 99; expressed by curves, 103; of some of the compounds of the metals, table of, 566, 567
Solute, 96
Solution, chemical, 97; definition of, 96; different from a compound, 97; equilibrium in, 257; homogeneous, 96; saturated, 98; supersaturated, 99
Solutions, 96; boiling point of, 103; classes of, 100; electrolysis of, 104; freezing point of, 103
Solvay, 427; portrait of, Fig. 250
Solvay process for soda, 427
Solvent, definition of, 96
Specific gravity, definition of, 81
Spectroscope, 226
Spectrum, 226
Speed of reaction and catalysts, 92
Sphalerite, 457
Spiegeleisen, 538
Spontaneous combustion, 44
Spray, lime-sulfur, 267
Stainless steel, 491
Stains, removal of, 499
Stalactites, 443
Stalagmites, 443
Standard, for molecular weights, 112; of valence, 159
Standard conditions, 65
Standard pressure, 65, 561
Stannic chloride, 522

Stannous chloride, 522
Stannous ions, reducing action of, 522
Starch, 376; action of hydrochloric acid on, 376; action of iodine on, 302; granules of, 377
Stassfurt salts, 430
State, colloidal, 339; combined and free, 25; nascent, 184
States of matter, 62
Staybright steel, 491
Stearic acid, 393
Stearin, 394; production of, from olein, 396
Steel, 487; electrothermal metallurgy of, 490; hardening of, 490; nickel, 497; production of, 490; properties of, 490; stainless, 491; staybright, 491; tempering of, 490; titanium, 543; vanadium, 543
Steel alloys, 491
Stellite, 497
Sterling silver, 512
Stibnite, 311
Stone, artificial, 336
Storage battery, 525
Stove polish, 137
Strength of acids and bases, 215
Strontium, 449; salts of, 449
Structural formula, 162
Structure of the atom, 165; how found, 169
Strychnine, 384
Substances, definition of, 21
Sucrose, 372; chemical conduct of, 374; refining of, 373
Sugar, beet, 372; cane, 372; grape, 376; inversion of, 374; invert, 374; maple, 373; milk, 374
Sugar of lead, 391, 526
Sulfate ion, test for, 282, 421
Sulfate radical, 203
Sulfates, 282; solubility of, 421
Sulfide ion, test for, 270
Sulfides, 267, 269; in lime-sulfur spray, 269; solubility of, 421; uses of, in analysis, 269
Sulfites, 277
Sulfur, 262; chemical conduct of, 266; distillation of, 264; extraction of, 263; flowers of, 264; monoclinic, 265; physical properties of, 264; plastic, 266; prismatic, 265; rhombic, 265; roll, 264; uses of, 266; varieties of, 265
Sulfur dioxide, 273; chemical conduct of, 274; in refrigerators, 275; preparation of, 274; uses of, 274
Sulfur in living matter, 263
Sulfur in plant growth, 318
Sulfur trioxide, 277
Sulfur waters, 269
Sulfuric acid, 277; action of, on metals, 280; action of, on salts, 281; an oxidizing agent, 280; chamber process for manufacture of, 279; contact process of manufacture of, 278; dehydrating action of, 281; manufacture of, 278; reduction of, 274; salts of, 282
Sulfuric anhydride, 277
Sulfurous acid, 275; properties of, 276; salts of, 277
Sulfurous anhydride, 273
Supersaturated solution, 99
Suspensions, 97
Sylvite, 430
Symbols, 26; meaning of, 120
Symbols and atoms, 26
Synthesis, method of, 85

Table, of densities and melting points of some common elements, 567; of electrochemical series, 216, 568, facing the inside back cover; of elements, inside back cover; of pressure of aqueous

vapor, 567; of relation between English and metric constants, 568, facing the inside back cover; of solubilities, 566, 567; of weights and boiling points of various gases, 568, facing the inside back cover
Talc, 453
Tar in road-making, 403
Tartaric acid, 393
Temperature, absolute scale of measuring, 562, 563; centigrade scale of measuring, 560; Fahrenheit scale of measuring, 560; solubility varies with, 101; standard, 65
Tempering steel, 490
Temporary hardness, 479
Terra cotta, 336
Test, flame, 435
Textile fibers, 379
Theories, 174; uses of, 66
Theory, atomic, 116; value of, 217
Thermite, 466
Thermometers, 77, 559; comparison of Fahrenheit and centigrade scales, 560
Thermos bottle, 235
Thomson, J. J., 294, 295; portrait of, Fig. 160
Thorium, radioactive, 554
Tin, 519; alloys of, 527; block, 519; chemical conduct of, 520; compounds of, 522; metallurgy of, 520; properties of, 519; uses of, 521; valences of, 522
Tin disease, 520
Tin foil, 520
Tin plate, 521
Tinstone, 519
Tires, manufacture of, Fig. 272
Titanium, 543
Titanium oxide, 543
Titanox, 527, 543
T. N. T., 402
Toluene, 402
Tooth powder, 441
Topaz, Oriental, 466
Transmutation, 4
Trinitrotoluene, 402
Trivalent atoms, 159
Tungsten, 543
Tungsten carbide, 497
Tungsten steel, 491
Tungsten wire, 543
Turnbull's blue, 496
Turpentine, 528
Tuyères, 485
Tyndall cone, 341
Type metal, 313, 527
Typhoid fever and impure water, 79

Ultramicroscope, 341
Ultraviolet light, 509
Univalent atoms, 159
Undercooled liquids, 69
Uranium, 547; the parent of radium, 549, 551; radioactive, 551
Uranium oxide, 544
Urea, 409

Valence, 158; application of, 160; atoms of no, 170; and atomic structure, 173; explanation of, 162; illustration of, 160; in periodic families, 291; method of representing, 161; negative, 173; of atoms, 158; of radicals, 204; positive, 173; standard of, 159; variable, 161, 173
Valence bonds, 161
Valence electrons, 173
Valences, table of, 162
Vanadium, 543; compounds of, as catalysts, 278
Vanadium steel, 491, 543
Vapor pressure of water, 564, 567
Vaporization, 71; heat of, 72
Vapors, 71
Varnish, 528

Vaseline, 352
Ventilation, 233
Vermilion, 511
Vinegar, 391; distilled, 393; malt, 393; manufacture of, 392; sugar, 393
Vitamins, 406; sources of, 408
Vitriol, blue, 282, 507; green, 492; oil of, 277; white, 457
Volatile matter, 139
Volumes of gases, problems based on, 127
Vorce cell, 180
Vulcanization, 459

Water, 76; analysis of, 84; bacteria in, 476; catalytic action of, 77; chemical conduct of, 77; composition of, 84; composition of, by volume, 87; derivation of formula of, 121; distillation of, 79; electrolysis of, 35, 215; impure, 78; mineral matter in, 78; physical properties, 76; purification of, 78, 476; purification of, by sand filtration, 477; purification of, by sulfates, 478; purification of, by chlorine, 477; sulfur, 269; synthesis of, by volume, 85; synthesis of, by weight, 88; vapor pressure of, 564; weight of 1 cc., 77
Water gas, 361
Water glass, 327
Water of crystallization, 78
Water of hydration, 78
Waters, hard, 478
Weights, gram-atomic, 125; gram-molecular, 125; of 1 liter of each of the common gases, 568, facing the inside back cover
Welding with aluminum, 465
Whisky, 386
White lead, 526
White vitriol, 457
Window glass, 332
Wines, 386
Wood, destructive distillation of, 139; preservation of, 457
Wood alcohol, 384
Wood's metal, 313
Wool fiber, 379
Wrought iron, 487

X rays, 547
Xenon, 226; in air, 229

Yeast, 386

Zeolite, 480
Zeolite process for softening water, 480
Zeppelins, 51; *see also* frontispiece
Zinc, 455; action of nitric acid on, 245; metallurgy of, 456; mossy, 455; occurrence of, 456; use of, in extracting silver, 513; uses of, 456
Zinc chloride, 457
Zincite, 456
Zinc oxide, 456
Zinc sulfate, 457
Zinc sulfide, 457
Zinc white, 457
Zircite, 543
Zirconium, 543
Zirconium oxide, 543
Zymase, 386, 387

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REFERENCE TABLES

WEIGHT IN GRAMS OF 1 LITER OF VARIOUS GASES UNDER STANDARD CONDITIONS, AND BOILING POINTS UNDER 760-MILLIMETER PRESSURE

Name	Weight of 1 Liter	Boiling Point	Name	Weight of 1 Liter	Boiling Point
Acetylene . . .	1.1621	−83.6°	Hydrogen chloride	1.6398	−85.0°
Air	1.2930		Hydrogen sulfide	1.5392	−59.6°
Ammonia . .	0.7708	−33.3°	Methane	0.7168	−161.4°
Argon.	1.7824	−185.7°	Nitric oxide. . .	1.3402	−151.0°
Carbon dioxide.	1.9768	*	Nitrogen	1.2506	−195.8°
Carbon monoxide	1.2504	−192.0°	Nitrous oxide . .	1.9777	−89.5°
Chlorine . . .	3.214	−34.6°	Oxygen	1.4290	−183.0°
Helium	0.1785	−268.9°	Sulfur dioxide . .	2.9266	−10.0°
Hydrogen . . .	0.08987	−252.7°			

ELECTROCHEMICAL SERIES

1. Lithium
2. Potassium
3. Sodium
4. Calcium
5. Magnesium
6. Aluminum
7. Manganese
8. Zinc
9. Chromium
10. Iron
11. Cadmium
12. Cobalt
13. Nickel
14. Lead
15. Tin
16. Hydrogen
17. Copper
18. Antimony
19. Bismuth
20. Arsenic
21. Mercury
22. Silver
23. Platinum
24. Gold

RELATION BETWEEN ENGLISH AND METRIC CONSTANTS

1 pound (troy) = 373.24 grams
1 ounce (troy) = 31.10348 grams
1 pound (avoirdupois) = 453.59 grams
1 ounce (avoirdupois) = 28.3495 grams
1 kilogram = 2.67923 pounds (troy)
1 kilogram = 2.20462 pounds (avoirdupois)
1 liter = 1.05668 United States liquid quarts
1 gallon = 3.78543 liters
1 cubic centimeter = 0.0610 cubic inch
1 cubic inch = 16.3872 cubic centimeters
1 cubic foot = 28,320 cubic centimeters
1 centimeter = 0.3937 inch
1 meter = 39.37 inches

1 cc. of water at its temperature of greatest density (4° C.) weighs approximately 1 g. For all ordinary purposes, therefore, 1 cc. of water may be regarded as weighing 1 g.

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*Under a pressure of 1 atmosphere, carbon dioxide vaporizes without melting. If subjected to a pressure of 5.2 atmospheres, it melts at − 56.6°.

TABLE OF THE CHEMICAL ELEMENTS, INCLUDING THEIR SYMBOLS, THEIR ATOMIC NUMBERS, AND THEIR ATOMIC WEIGHTS

NAME	SYMBOL	ATOMIC NUMBER	ATOMIC WEIGHT	NAME	SYMBOL	ATOMIC NUMBER	ATOMIC WEIGHT
Actinium	Ac	89	—	1,2 Mercury ✓	Hg	80	200.61
3 Aluminum ✓	Al	13	26.97	6 Molybdenum ✓	Mo	42	96.0
3,5 Antimony ✓	Sb	51	121.77	Neodymium	Nd	60	144.27
0 Argon ✓	A	18	39.94	Neon	Ne	10	20.183
3,5 Arsenic ✓	As	33	74.93	2,3 Nickel ✓	Ni	28	58.69
2 Barium ✓	Ba	56	137.36	1,2 Nitrogen 3,4,5 ✓	N	7	14.008
Beryllium	Be	4	9.02	Osmium	Os	76	190.8
3 Bismuth ✓	Bi	83	209.00	2 Oxygen ✓	O	8	16.000
3 Boron ✓	B	5	10.82	Palladium	Pd	46	106.7
1 Bromine ✓	Br	35	79.916	3,5 Phosphorus ✓	P	15	31.02
2 Cadmium ✓	Cd	48	112.41	2,4 Platinum ✓	Pt	78	195.23
2 Calcium ✓	Ca	20	40.07	Polonium	Po	84	210.(?)
4 Carbon ✓	C	6	12.00	1 Potassium ✓	K	19	39.10
Cerium	Ce	58	140.13	Praseodymium	Pr	59	140.92
Cesium	Cs	55	132.81	Protoactinium	Pa	91	—
1 Chlorine ✓	Cl	17	35.457	2 Radium ✓	Ra	88	225.97
3,6 Chromium ✓	Cr	24	52.01	Radon	Rn	86	222.
2,3 Cobalt ✓	Co	27	58.94	Rhenium	Re	75	188.7
Columbium	Cb	41	93.1	Rhodium	Rh	45	102.91
1,2 Copper ✓	Cu	29	63.57	Rubidium	Rb	37	85.44
Dysprosium	Dy	66	162.46	Ruthenium	Ru	44	101.7
Erbium	Er	68	167.64	Samarium	Sm	62	150.43
Europium	Eu	63	152.0	Scandium	Sc	21	45.10
1 Fluorine ✓	F	9	19.00	Selenium	Se	34	79.2
Gadolinium	Gd	64	157.26	4 Silicon ✓	Si	14	28.06
Gallium	Ga	31	69.72	1 Silver ✓	Ag	47	107.880
Germanium	Ge	32	72.60	1 Sodium ✓	Na	11	22.997
3 Gold 1,3 ✓	Au	79	197.2	2 Strontium ✓	Sr	38	87.63
Hafnium	Hf	72	178.6	2,4,6 Sulfur ✓	S	16	32.06
Helium	He	2	4.002	Tantalum	Ta	73	181.5
Holmium	Ho	67	163.5	Tellurium	Te	52	127.5
1 Hydrogen ✓	H	1	1.008	Terbium	Tb	65	159.2
Illinium	Il	61	—	Thallium	Tl	81	204.39
Indium	In	49	114.8	Thorium	Th	90	232.12
1 Iodine ✓	I	53	126.932	Thulium	Tm	69	169.4
Iridium	Ir	77	193.1	2,4 Tin ✓	Sn	50	118.70
2,3 Iron ✓	Fe	26	55.84	Titanium	Ti	22	47.90
Krypton	Kr	36	82.9	Tungsten	W	74	184.0
Lanthanum	La	57	138.90	Uranium	U	92	238.14
1,2 Lead ✓	Pb	82	207.22	Vanadium	V	23	50.96
1 Lithium ✓	Li	3	6.940	Xenon	Xe	54	130.2
Lutecium	Lu	71	175.0	Ytterbium	Yb	70	173.6
2 Magnesium ✓	Mg	12	24.32	Yttrium	Y	39	88.92
2,4,7 Manganese ✓	Mn	25	54.93	2 Zinc ✓	Zn	30	65.38
Masurium (?)	Ma	43	—	Zirconium	Zr	40	91.22

-ide = 0 oxygen

-ite = 2 oxygens